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At-Sea Incineration of Organochlorine Wastes Onboard the M/T Vulcanus

TRW, Inc, Redondo Beach, Calif

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

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ABSTRACT

This report describes the incineration of 4100 tonnes of organochlorine wastes by the M/T Vulcanus in an EPA designated burn area in the Gulf of Mexico under a special permit granted by Region VI of the EPA. The wastes, containing 63% chlorine, orginated from manufacturing processes conducted by the Shell Chemical Co., Deer Park, Texas, and was loaded onto the Vulcanus at the Shell Deer Park facility.

The incineration process was monitored by a field sampling team from TRW, Redondo Beach, Ca. Waste destruction efficiencies and total combustion efficiency were determined by five methods, each with separate means of sampling, analysis, and calculation. Incinerator efficiencies of at least 99.9% were observed, at an average waste feed rate of 22 tonnes/hr. The process was carried out at a flame temperature averaging 1535°C and at dwell times calculated to be 0.9 seconds.

An automatic waste shut off system was incorporated into the incineration process, and was pre-set so as to shut down the flow of waste if the flame temperature should drop below 1200°C. The temperature of the process was monitored directly by an optical pyrometer for flame temperature and indirectly by thermocouples which measured wall temperature and which were statistically correlated with the flame temperature.

PREFACE

Organochlorine incineration on board the M/T Vulcanus operating in the Gulf of Mexico was accomplished under provisions of an Environmental Protection Agency Special Permit. Thermal destruction of such wastes at sea is a relatively new disposal method in the United States. The purpose of sampling and monitoring approximately one-third of the total waste destroyed during this incineration operation was twofold. First, there was a definite need to test the suitability and reliability of a comprehensive stack gas sampling apparatus and an on-line monitoring instrumentation system. And secondly, data was required in support of developing United States guidelines and regulations for new incineration ships. It was not the intent of this work to insure compliance with permit operating conditions for Gulf of Mexico incineration activity.

Successful accomplishment of this effort was due to the assistance and cooperation of a large number of individuals and their respective organizations. Equipment design and development, definition of sampling requirements and the acquisition of samples and subsequent analysis was accomplished by personnel from the Applied Technology Division and the Environmental Engineering Division of TRW, Inc., Redondo Beach, California. Engineering liaison to adapt test equipment on-board the Vulcanus was facilitated by the management of Ocean Combustion Services, B.V., of The Netherlands. Subsequent installation of this equipment as well as the acquisition of data could only have been accomplished with the complete cooperation of the ship's officers and crew.

Technical direction, assistance and planning of the program's conceptual design and implementation was received from a number of agencies within the U. S. Government. These include the U. S. Environmental Protection Agency's Oil and Special Materials Control Division (OSMCD), Washington, D.C.; Industrial Environmental Research Laboratory (IERL), Research Triangle Park, North Carolina; and the Regional Office, Region IV, Dallas, Texas. Guidance in installing equipment on the Vulcanus to conform with U. S. maritime regulations was provided by the U. S. Coast Guard, Headquarters, Washington, D.C.

Representatives of the Shell Chemical Company, Deer Park, Texas, provided waste samples for preliminary analysis prior to the burn as well as technical details regarding their original sampling and monitoring work on board the Vulcanus in 1974. Personnel of Arthur D. Little, Inc., Cambridge, Massachusetts, provided consultation regarding sample preparation and analysis.

The authors are indebted to the many individuals of all these organizations for their contributions and cooperation.

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1. INTRODUCTION AND SUMMARY

Thermal destruction of chlorinated hydrocarbon wastes at sea is a relatively new disposal technique for wastes generated in the United States. In late 1974, organochlorine wastes were incinerated in the Gulf of Mexico for the first time by the Motor Tanker (M/T) Vulcanus. This effort, monitored by the U. S. Environmental Protection Agency (EPA), provided an initial technical basis for concluding that at sea incineration was a viable alternative to other means of disposal using land based facilities (Reference 1).

A second incineration program, again burning organochlorine waste, was performed on board the M/T Vulcanus during the period 5 through 13 March, 1977. This second Gulf of Mexico incineration afforded an opportunity to employ recent technology for monitoring and assessing the environmental effectiveness of this disposal process. The purpose of this test work was to evaluate the adequacy and reliability of the monitoring and comprehensive sampling system. Previously, these systems had been utilized on land-based incineration facilities (References 2, 3). The ability to make such a system reliably operate in the more harsh environment encountered during at sea incineration remained to be demonstrated. A second equally important objective for the current program was acquisition of sufficiently comprehensive data to support developing at sea incineration regulations and guidelines for future new incinerator vessels.

The scope of activities for this work included design and preparation of the stack gas sampling and monitoring apparatus, development of a sampling and analysis protocol, acquiring samples and monitoring waste effluent during incinerator operation, as well as analysis of these samples followed by evaluation of the results. This report presents results obtained during the EPA sponsored monitoring and sampling program.

During the sampling and monitoring operations on board the M/T Vulcanus in March, 1977, approximately 4100 tonnes (metric tons) of Shell Chemical Company wastes were incinerated. This was accomplished under Special Permit No. 75000008E granted to the Shell Development Company by Region VI of the Environmental Protection Agency (Reference 4). This represented about one-third of the total waste destroyed as allowed by the permit conditions. The site of the combustion, as fixed by the permit, lay in the Gulf of Mexico within a rectangle

defined by the following coordinates:

Latitude	Longitude
27° 06' 12" N	93° 24' 15" W
26° 32' 24" N	93° 15' 30" W
26° 19' 00" N	93° 56' 00" W
26° 52' 40" N	94° 04' 40" W

At its nearest point to land, this site is approximately 130 miles to the south of Sabine Pass, Texas.

The wastes burned were produced as by-products in the manufacture of allyl chloride, epichlorohydrins, dichloroethane and vinyl chloride at Shell Chemical Company's Deer Park, Texas, plant. The material consisted primarily of low molecular weight chlorinated aliphatics and had a gross heat content of 3,860 kcal/kg (6,950 Btu/lb).

Sampling operations utilized a high volume EPA Source Assessment Sampling System (SASS) with a sampling rate of 0.095 cubic meters per minute. This sampling train was used to trap and remove organic vapors from the stack effluent. Sample acquisition was by a remotely actuated, water-cooled stainless steel probe capable of traversing the starboard incinerator stack diameter of 3.4 meters. During stack sampling operations, incineration effluent products were simultaneously monitored for total hydrocarbons, carbon monoxide and dioxide, nitrogen oxide and dioxide as well as oxygen concentration. These parameters were measured in real time to monitor the overall combustion efficiency of the incinerator. SASS train components were subsequently analyzed in detail by laboratory methods. The purpose of these analyses was to determine how effectively the incineration process destroyed constituents in the organochlorine waste feedstock.

The waste was burned at an average rate of 22 tonnes per hour or approximately 11 tonnes per hour for each incinerator. Total elasped burn time was 186 hours and 45 minutes. The average flame temperature was 1535°C as determined by optical pyrometer measurements. Under these conditions, a combustion gas residence time in the incinerator was calculated to be approximately 0.9 seconds.

Six waste incineration sampling tests (I through VI) and one background test (VII) burning fuel oil alone were conducted. Because sampling tests were longer and generally more successful for tests IV through VII, these test data and samples were analyzed more intensively. Data from the on-line analyzers were used to calculate combustion efficiency while sampling operations were in progress. Analytical results as well as on-line total hydrocarbon measurements provided the basis for calculating waste destruction efficiencies. Five efficiencies were determined, each with separate means of sampling, analysis and calculation. These five

destruction efficiency terms are listed and defined in Table 1-1. The resulting destruction efficiency values are presented in Table 1-2 for tests IV through VII. The latter was the background or baseline test using fuel oil.

TABLE 1-1. DEFINITION OF DESTRUCTION EFFICIENCY TERMS

Destruction Efficiency Term	Method of Efficiency Calculation	Description of Method
DE_{CE}	$\left(1 - \frac{CO_2 \text{ rate}}{CO_2}\right) \times 100$	Overall combustion efficiency based on carbon dioxide and carbon monoxide concentrations. CO_2 and CO were measured by continuous on-line monitors on board the Vulcanus.
DE_{THC}	$\frac{\text{THC fed} - \text{THC from on-line monitor}}{\text{THC fed}} \times 100$	Total organic destruction efficiency based on total hydrocarbons (THC) measured by a continuous on-line monitor on board the Vulcanus.
DE_{GGHC}	$\frac{\text{THC fed} - \text{THC in grab gas sample}}{\text{THC fed}} \times 100$	Total organic destruction efficiency based on total hydrocarbons measured in the Tedlar bag grab gas samples analyzed by GC/FID.
$DE_{SC_3Cl_3}$	$\frac{C_3Cl_3 \text{ fed} - C_3Cl_3 \text{ in SASS sample}}{C_3Cl_3 \text{ fed}} \times 100$	Waste destruction efficiency based on trichloropropane (major waste constituent) found in SASS train samples. Trichloropropane was identified and quantified by GC/MS.
$DE_{GGC_3Cl_3}$	$\frac{C_3Cl_3 \text{ fed} - C_3Cl_3 \text{ in grab gas samples}}{C_3Cl_3 \text{ fed}} \times 100$	Waste destruction efficiency based on trichloropropane found in grab gas samples by GC after linear concentration.

TABLE 1-2. SUMMARY OF CALCULATED DESTRUCTION EFFICIENCIES

	Test Number			
	IV WASTE	V WASTE	VI WASTE	VII BACKGROUND
DE_{CE}	99.98 %	99.96%	99.97%	99.97%
DE_{THC}	99.991%	99.996%	99.996%	99.997%
DE_{GGHC}	99.996%	99.996%	99.997%	99.999%
$DE_{SC_3Cl_3}$	99.9%	99.92%	99.9%	-
$DE_{GGC_3Cl_3}$	>99.999%[a]	>99.999%[b]	>99.999%[b]	-

a) Waste constituents not detected
b) Based on trace quantity of trichloropropane found

The results of these tests indicate that incineration performance on the M/T Vulcanus was consistently greater than 99.9 percent for both waste and total organic destruction efficiency. These results are comparable to land-based incinerator performance with chlorinated waste materials (References 2, 3). Trace levels of known waste constituents such as trichloropropane (0.1 to 0.6 mg/m^3) were found in the effluent gases. Additionally, low ppm and ppb levels of chlorinated and alkyl substituted benzene compounds were found in some samples. These materials could have been in the waste feed at levels which were too low to make confirmed indentification, or they may have been masked by other constituents during the waste characterization. This identification level was estimated to be less than 0.5 percent in the waste. A specie at 0.5 percent, if totally undestroyed in the incinerator, would create an emission level of approximately 700 ppm which is about 1000 times the amount actually found. Thus, efficient destruction of these compounds is still indicated if they are indeed waste constituents at a 0.5 percent level. Two other possible sources of these materials may be postulated. These compounds may have been by-products of the combustion, having been synthesized in the process or the materials may have been the result of a chlorination of otherwise non-chlorinated materials within the sampling train.

An interesting and significant result derived from the on-line monitoring data was that a fixed position effluent gas sampling probe would have sufficed to insure that incinerator combustion efficiency was always equal to or greater than 99.9 percent. Potential wall effects on the combustion gas composition were apparently eliminated at distances greater than 15 cm from the inside incinerator wall surface.

The Vulcanus incinerators were effective in destroying this organochlorine waste material. The sampling (SASS) train, although advantageous for acquiring large volume samples, was of marginal utility due to the use of stainless steel construction in many components. Corrosion was a continual problem area due to the high (approximately 6-8 percent) hydrochloric acid (HCl) content in the combustion products. An all glass sampling train would eliminate this problem. The on-line analyzer system was adequate for the monitoring program. Frequent calibration and maintenance was, however, required to keep the system on-line at the desired times. Most difficulty was experienced with the CO, CO_2 and NO analyzers. Although these instruments were designed for process stream measurement (for instance, utilities, cement kilns, etc.), it is doubtful that the extremely hostile environment of at sea incineration was ever considered in their original design specifications. In particular, the shock and vibration modes encountered at sea are somewhat unique. Equally significant was the salt air environment and high HCl concentration in the combustion gas stream. The monitoring system employed was adequate for this experimental work. In future applications of this type, more attention must be given to the technical details which will reduce maintenance and increase instrument reliability. This appears entirely feasible within current technology.

Cooperation and assistance by the ship's crew was excellent. Incinerator controls and instrumentation was sufficient. Additional incinerator wall temperature thermocouples and readouts would be desirable for purposes of redundancy since existing thermocouples cannot be replaced during furnace operations. Waste feed rates can only be determined via tank depletion rates based upon depth soundings. A remote gaging system would be advantageous from the standpoint of handling hazardous wastes especially of a volatile nature. Similarly, waste flow metering equipment would be useful to acquire real time data as opposed to time averaged data as at present. This is, however, an admittedly very difficult technical requirement to implement.

No significant incidents related to safety were experienced during sampling and monitoring operations. In retrospect, adequate scaffolding should have been installed around the traversing probe. Replacement of the probe at sea constituted a safety hazard to the sampling crew. Subsequent incineration test programs at sea should include development of a definitive, formal safety plan. Although oral safety briefings were conducted, no formal written safety document was employed during this test. Because of the unique working environment at sea, a safety plan is advisable in the future.

Ship-to-shore radio communications were at best only marginal. The precise technical reasons for this situation are unknown. To facilitate subsequent test programs, a communications plan should be developed that establishes pre-arranged reporting times and format, and insures equipment compatibility.

And finally, an at sea sampling and monitoring operations plan must coordinate with all interested or associated government organizations such as U. S. Customs and the U. S. Coast Guard. When properly briefed, their assistance is most helpful.

2. DESCRIPTION OF THE M/T VULCANUS

2.1 VESSEL - GENERAL LAYOUT

The M/T Vulcanus, originally a cargo ship, was converted in 1972 to a chemical tanker fitted with two large incinerators located at the stern of the vessel. The vessel meets all applicable requirements of the Inter-governmental Maritime Consultative Organization (IMCO) concerning transport of dangerous cargo by tanker. Figure 2-1 shows a picture of the vessel and table 2-1 gives some of the ship's specifications. Both the picture and the table were furnished by Ocean Combustion Services, B. V., Rotterdam, The Netherlands, who manage the vessel.

Because of her size - an overall length of 102 meters, a beam of 14.4 meters, and a maximum draft of 7.4 meters - the Vulcanus is able to operate worldwide. Two diesel engines drive a single propeller to give cruising speeds of 10 to 13 knots. Her crew numbers 16; ten to operate the vessel and six to operate the incinerators.

2.2 TANKS AND PUMPS

In this double-hull, double-bottom vessel, the waste is carried in 15 tanks which lie within the inner hull (Figure 2-2). The tanks range in size from 115 to 574 cubic meters (cu m), with the overall waste capacity being 3,503 cu m. Tanks are filled through a manifold on deck using a dockside loading pump. During normal operation the waste tanks can be discharged only through the incinerator feed system. There is, however, provision for discharging the cargo into the ocean if an emergency arises. The manner in which the piping system is constructed makes it possible for any tank to be connected to either incinerator and for cargo to be transferred from one tank to another.

The space between the two hulls is used for ballast. Ballast tanks may be filled with sea water and emptied independently as required to trim and balance the ship. Fuel oil is carried in tanks under and in the engine room. The engine room is separated from the cargo tanks by double bulkheads. The pump room and generator room are situated between the engine room and the waste tanks.

2.3 INCINERATOR SYSTEM

Waste is burned in two identical refractory-lined furnaces located at the stern of the ship. Each incinerator combustion chamber consists of two main sections, a combustion chamber and a stack, through which the combusting fluids pass sequentially (Figure 2-3). This dual chamber configuration, which is characteristic of most high intensity combustion

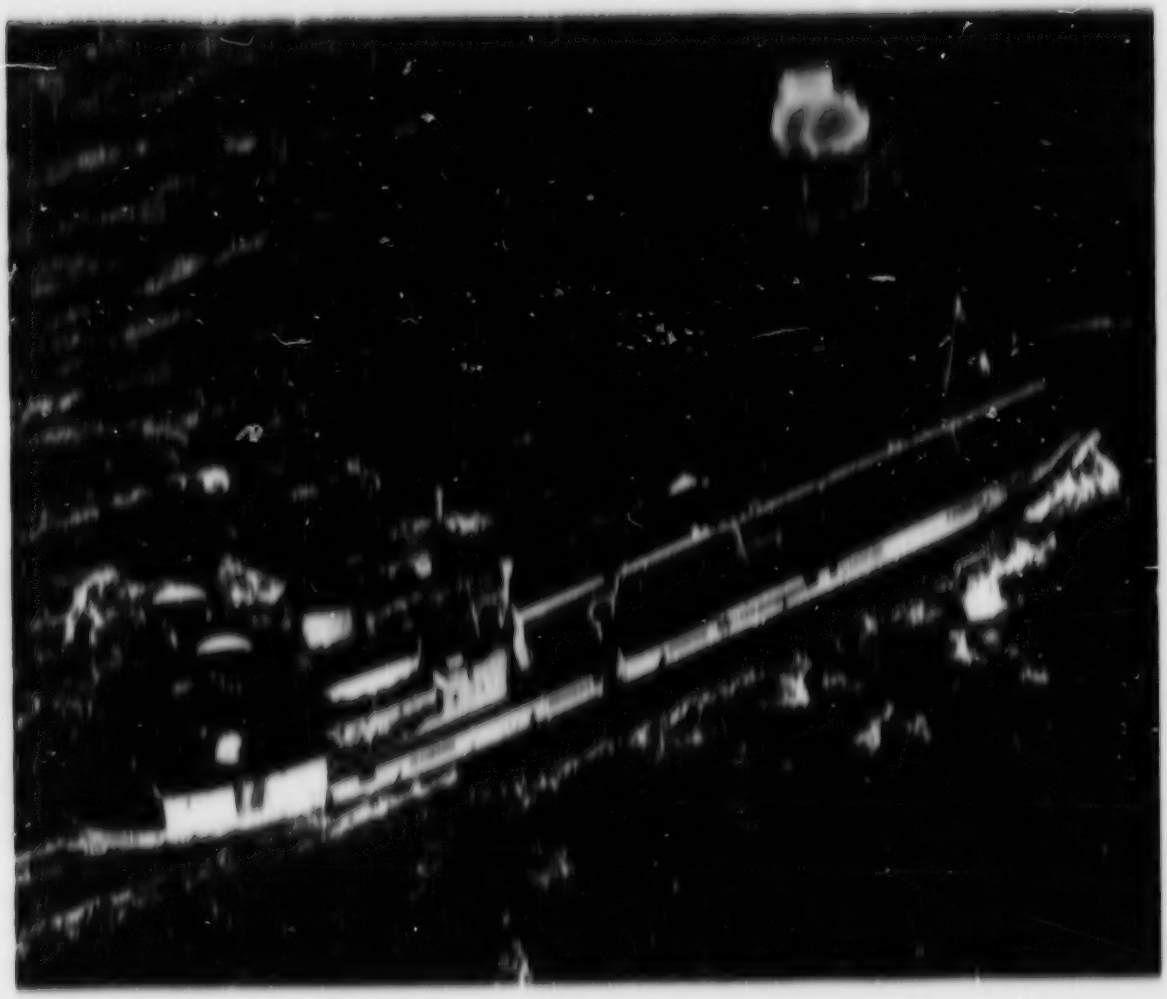

Figure 2-1. M/T Vulcanus - incineration vessel

systems, uses the first chamber for internal mixing and the second for adequate residence time. Each furnace has the following characteristics:

Overall Height	10.45 meters (m)
Combustion Chamber	
O.D.	5.5 m
I.D.	4.6 m
Stack (Top)	
O.D.	3.8 m
I.D.	3.4 m
Combustion Capacity (Max)	12.5 Tonnes/hour
Combustion Air	90,000 cu m/hour (maximum)
Burners (Saacke Type)	3
Volume	120 cu m
Residence Time:	0.9 sec at 1200°C (calculated)

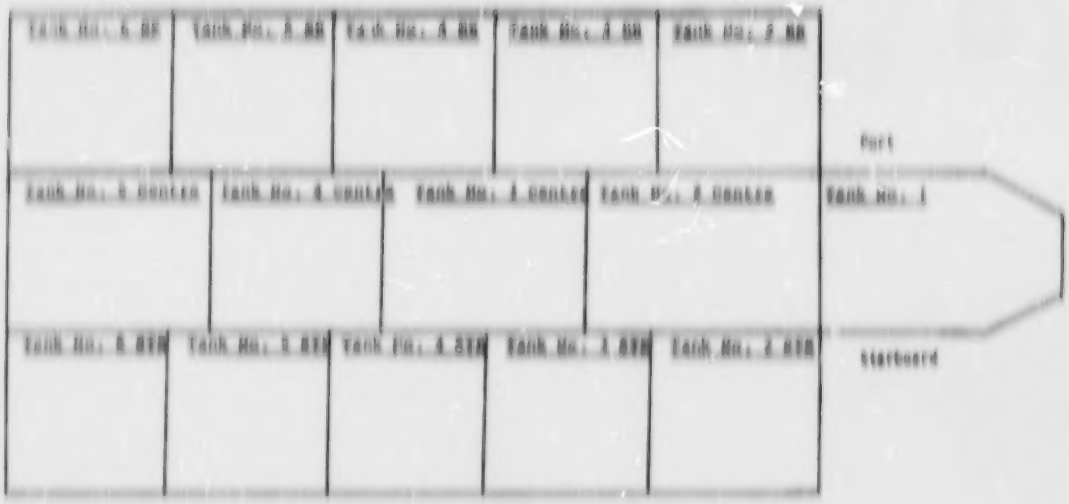

Figure 2-2. Tank layout schematic

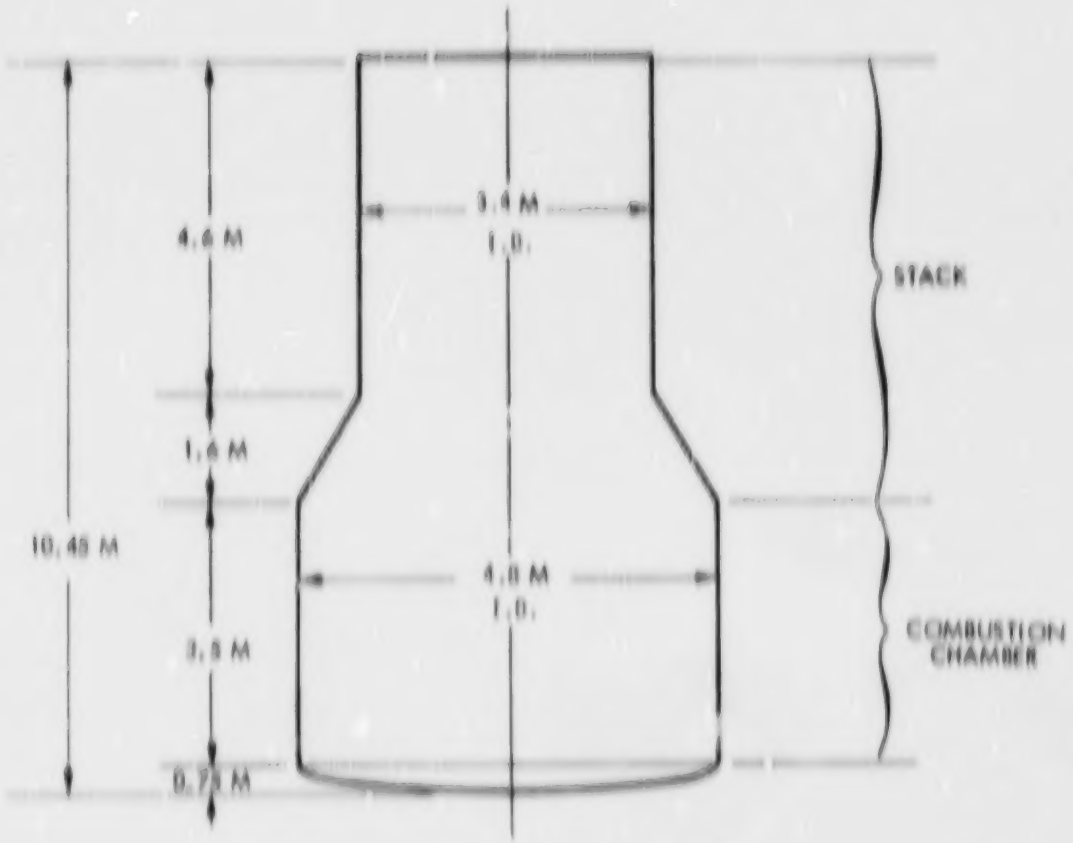

Figure 2-3. Incinerator configuration

TABLE 2-1. SPECIFICATIONS OF THE M/T VULCANUS

Length overall	101.95 meters
breadth	14.40 meters
Draft, maximum	7.40 meters
Deadweight	4,768 tonnes
Speed	10-13 knots
Tank capacity	3,603 cubic meters (cu m)
Number of tanks	15, ranging in size from 115 cu m to 574 cu m
Tank coating	No coating in tanks, pipes, pumps, etc. All equipment consists of low carbon steel
Loading equipment	Not available, but can be placed on board, if required
Hose connection	10.2, 15.2, and 20.3 centimeters (4, 6, 8 inches) in diameter
Safety equipment	Specially designed for this task and in accordance with latest regulations of IMCO, Scheepvaart-Inspectie (the Hague)
Waste to be processed	Must be liquid and pumpable. May contain solid substances in pieces up to 5 centimeters in size. Must not attack mild steel
Incinerators	2
Incinerator Capacity	up to 25 tonnes/hour

Air for the combustion is supplied by large fixed speed blowers with a rated maximum capacity of 90,000 cubic meters per hour for each incinerator. Adjustable vanes are incorporated in the combustion air supply system which when deflected, increase system pressure drop and reduce the flow rate. Although no instrumentation is installed to monitor air flow rate, normal operation is stated by the ship's crew to be between 75,000 and 80,000 cubic meters per hour.

Liquid wastes are fed to the combustion system by means of electrically driven pumps. Upstream of each burner supply pump is a device (Gorator) for reducing the solids in the waste to a pumpable slurry. The Gorator also acts as a mixing pump by recirculating the waste through the waste tank. Power for the blowers, pumps and other parts of the incinerator system is supplied by two diesel-generators with a total capacity of 750 KW at 440 volts and 60 Hertz.

Three burners of the vortex type are located on the same level at the periphery of each furnace near its base. The burners are of a rotating cup, concentric design, which deliver waste or fuel oil through a central tube to an atomization nozzle, where it meets high velocity air delivered through an annulus. The burners are directed as shown in Figure 2-4.

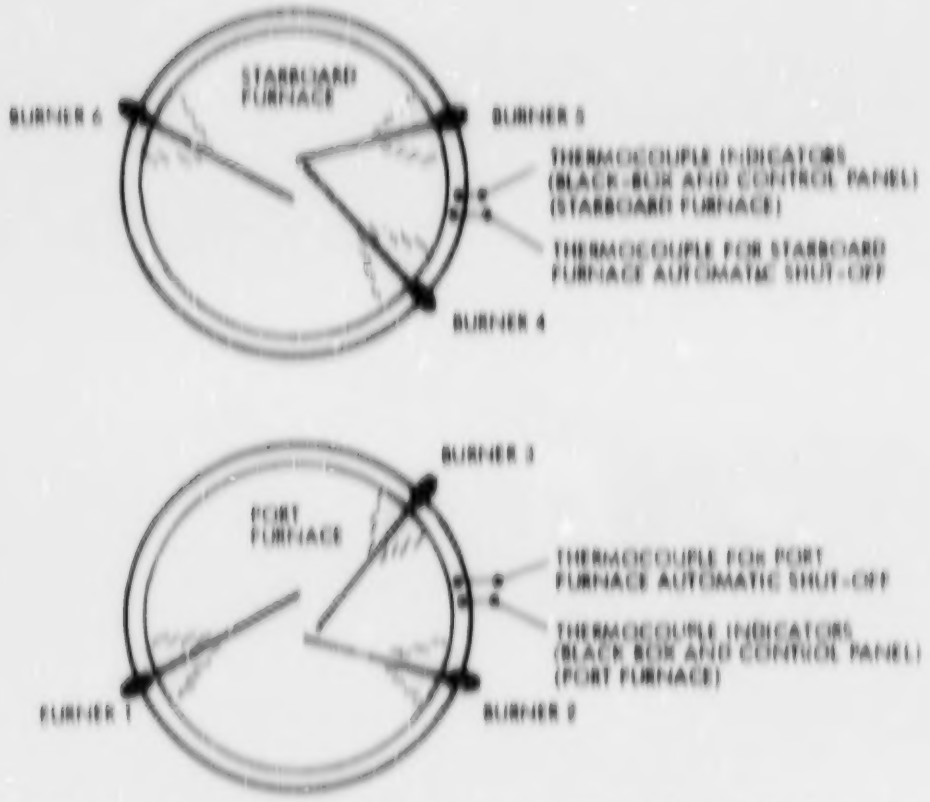

Figure 2-4. Incineration system - burner and thermocouple locations

Periodically the burners require cleaning. The burners are normally cleaned one at a time with the remaining two burners firing waste during the cleaning. This is easily accomplished because the burners are readily accessible. Each burner has a vertical pivot or hinge so that it can be swung out of the furnace. The opening left by this operation is temporarily closed by a cover. The burners are cleaned by a metal tool which is pushed through the burner. Three-way valves are utilized on each burner providing waste feed, fuel oil feed or a shutoff condition. Waste and fuel oil cannot be valved into a burner simultaneously; however, alternate burners could be operated with fuel and waste to achieve higher combustion temperatures if necessary.

2.4 RECORDING AND CONTROL EQUIPMENT

2.4.1 Waste Measurements

The measurement of waste in the tanks during this burn was accomplished by sounding the depth of waste in each tank with a tape. In order to comply with U.S. Coast Guard requirements, a new measuring system which is sealed to prevent vapors from escaping into the ambient air was installed at the completion of the burn.

2.4.2 Wall Temperature Measurements

Temperatures during operation of the incinerators are measured by two platinum-platinum/10% rhodium thermocouples in each incinerator. Each pair is located in a well opposite one of the burners. One thermocouple is located approximately 1.3 centimeters from the inside surface of the refractory lining. This thermocouple provides temperature information to the automatic waste shutoff system and is referred to as the "controller" thermocouple in the Appendix B data tables. A second thermocouple approximately 4 centimeters from the inner surface of the firebrick is referred to as the "indicator" because it provides temperature information to a panel located in the incinerator control room and to a panel located on the bridge. The Appendix B data table refers to the bridge panel as the "black box." In addition, this control panel indicates the day, month and time, and has lamps which show the burners and pumps are operating.

The thermocouples used to feed the automatic waste shut off system and the recording equipment have been quite reliable and durable, according to personnel of the M/T Vulcanus. There were no known failures during the burn covered in this report.

The possibility of replacing a thermocouple during a burn was discussed. The opinion expressed by the operating personnel is that removal and replacement of a thermocouple in a furnace is not feasible while operating.

2.4.3 Emergency Automatic Waste Shut-off

For the March 1977 burns, an automatic waste cut-off system was used. This system, called the Plastomatic 2000 and supplied by Withoff-Phillips, Bremen, W. Germany, uses a thermocouple controlled, spring loaded, solenoid

actuated valve which shuts off waste to the burners when the temperature of the furnace drops below a pre-set selected temperature. During these tests the EPA required the shut off temperature to be set at 1200°C.

If the temperature in a furnace drops below the pre-selected minimum, a solenoid is de-activated, allowing a spring loaded valve to close, thus shutting off the flow of waste to the three burners of that furnace. The valve which is thus closed shuts the line in both directions. The waste pumps are also stopped at this time by cutting off power. A power failure or thermocouple burnout in the Plastomatic system would also shut off the flow of waste to the burners involved.

A demonstration of the action of the solenoid-actuated valve was set up by the Chief Electrician and Chief Engineer of the Vulcanus. A cutaway model of the valve was set up, the valve opened, and the solenoid activated electrically. The valve remained open. Upon breaking the electrical contact, the spring closed the valve rapidly and positively, preventing flow in either direction. The breaking of the electrical contacts simulated the action of the Plastomatic system if its thermocouple should indicate temperature lower than the one selected at the control panel. Similarly, a loss of power would shut off the waste flow to the furnace, and would prevent backflow of the waste.

If the system should function, i.e., shut off the waste flow, the pump which has been stopped and the valves which have been closed may be restarted after the cause has been identified and corrected and after the Plastomatic has been reset. It should be noted that procedures require restart and reestablishment of the desired temperatures using fuel oil before waste can be burned again.

As shown in the Appendix B data tables, the thermocouple providing wall temperature sensing to the automatic shutoff system ("controller" thermocouple) may also be utilized to indicate real time wall temperature measurements. This is accomplished by adjusting the controller from the shutoff temperature setting (in this instance, 1200°C) to increasingly higher temperature settings. When the adjusted setting is coincident with the actual temperature sensed by this thermocouple, the feed valve relay clicks. Observation of the pointer location with respect to the temperature scale on the dial provides a temperature reading. The waste shutoff system is not immediately activated since a time delay is incorporated in the electrical circuit. The pointer is then reset to the desired automatic shutoff temperature before the system can activate. The ability to record temperatures in this manner is useful in the event that the "indicator" wall temperature should fail during operation.

2.4.4 Special Equipment

Certain equipment, not usually found aboard chemical tankers, has been installed on the Vulcanus because of its particular type of operation. These items of equipment are:

Loran and Decca Navigational Aids: This equipment is needed in European waters (Decca) and United States waters (Loran) in order to assure precise location of the ship at all times. During the current trip, Loran was used to locate and keep the Vulcanus in the designated burn area.

Anemometer: This equipment measures the velocity and force of the wind. It is therefore useful in selecting an attitude of the ship during various wind conditions such that the plume may be directed away from the ship and its personnel.

Radio Communication: The Vulcanus is equipped with SSB (single side band) and DSB (double side band) radio for voice and code communication; MF (medium frequency) and SF (short wave) telegraphy; Marifoon (VHF) (all channels) for close in voice communication; and Semafoon (a private telephonic communication system).

Optical Pyrometer: A portable optical pyrometer was utilized during the test program to measure incinerator flame temperatures. These measurements were taken periodically (see Appendix B data tables) using a Leeds and Northrup Optical Pyrometer operating in the 6500 Å range.

3. TEST DESCRIPTION

This section presents the manner in which the sampling tests were carried out. It is divided into the following subsections, listed in order of discussion:

- Operational procedures.
- Sampling methods.
- Analysis techniques.
- Problems encountered.

The operational, sampling, and analysis procedures were designed and selected with consideration given to the nature of the waste. A preliminary survey sample of the waste material was acquired and analyzed prior to the final planning of the shipboard incineration test program. The waste was a low-viscosity, low-ash liquid with a gross heating value of 3,860 kcal/kg (6,950 Btu/lb). Its elemental composition was 30.01 percent carbon, 4.17 percent hydrogen, 0.012 percent nitrogen, 0.009 percent sulfur, 62.6 percent halogens (as chlorine), and 3.2 percent oxygen (by difference). GC/MS analysis showed the waste to consist nearly entirely of low molecular weight (2-3 carbons), chlorinated alkyl compounds with trace amounts of oxygenated chloroalkyl compounds. Samples of the waste material actually burned were taken on board the ship during the tests and the results of analyzing those samples are presented in Section 4.2.1.

3.1 OPERATIONAL PROCEDURES

Detailed operating and safety procedures were reviewed and approved prior to arrival of the TRW sampling team on board the M/T Vulcanus. Procedures and operating conditions were also recorded during the actual tests. Following are brief summaries of procedures and a test-by-test commentary on events that took place on the vessel.

3.1.1 Test Procedures

Sampling was conducted on the starboard incinerator. Two sample ports were available for probe insertion; however, safety considerations ruled out Port #2 (see Figure 3-1). Port #1, located above a burner and pointing toward the center of the incinerator, was used to obtain the combustion gas samples. During each test several points along this diameter were sampled since the probe could traverse the stack.

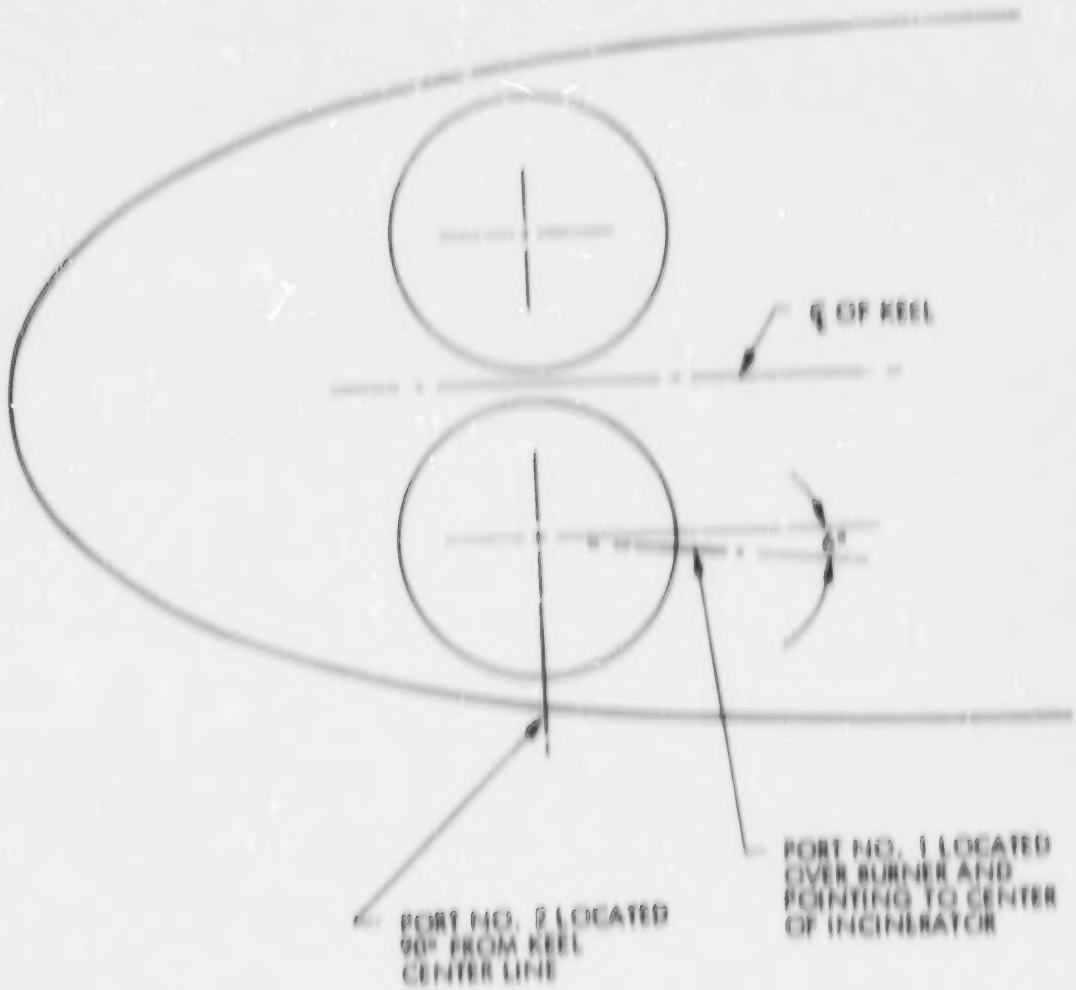

Figure 3-1. Sampling port locations

A total of seven sampling tests were conducted. The last test was for a background while only fuel oil was burned in the starboard incinerator. The basic procedure for each test was:

- Verify sampling system ready
  - Fill first two impingers with caustic solution
  - Fill last impinger with silica gel
  - Leak check the system
  - Fill impinger box with ice
- Verify on-line instrumentation ready
- Start sampling system

- Stabilize flow rates and temperatures in sampling system
- Activate on-line analyzer system
- Extended sampling duration
  - Process data acquisition
  - Effluent gas composition data acquisition
  - Effluent gas sampling
- Shutdown on-line analyzer
- Shutdown sampling system
- Recover and store samples

Each sampling test was scheduled to run from three to five hours.

3.1.2 Safety Procedures

Safety requirements for handling and operating the sampling trains and ancillary equipment were established and adhered to, including the following:

- Only authorized personnel were permitted in the sampling area during a test.
- Visual observation of the test system was maintained at all times during tests.
- Entry suits and Scot-Paks were available in the immediate area.
- Safety belts were used when working on the probe or probe mount.
- Sampling tests were performed only when weather conditions were favorable.

Safety procedures for operations of the Vulcanus crew are contained in Appendix C.

3.1.3 Test Commentary

Six sampling tests were conducted during the incineration of the organochlorine wastes and one background test with fuel oil. For convenience, the waste tests were conducted before the background test. Before starting waste combustion, the furnaces were heated to operating temperature by burning fuel oil. When the preselected temperature had been reached, the system was switched over to waste. Because a "cold"

furnace must be heated slowly in order to avoid cracking the refractory liner, the burners were turned on and off intermittently, in order to provide slower and more uniform heating. After preheating to operating temperature, changeover to waste was accomplished by switching each burner successively to waste. The effect on the temperature was small, a lowering of approximately 10-20°C being observed on the thermocouple dial on the control panel in the combustion room.

General observations of the incinerator operation were noted. The typical flame produced by the burners was bright, intense white, free of dark areas and free of sputtering. No black particulate matter was observed above the stack exit. The daytime appearance was one of heat convection above the incinerator. At night the gases above the incinerator were white against the black sky. Excursions of flames beyond the incinerator were not observed while waste was being burned. An occasional vibration was noted in the furnace. This condition appeared to be associated with burners which were being pushed to capacity. Backing off of the flow rate to the burner appeared to eliminate the condition. The phenomenon did not appear to correlate with any other parameters, i.e., time of day or night, ship speed, etc. A continual inspection of the incinerator burners was maintained by the Vulcanus personnel. Burners were cleaned periodically, usually yielding a black coke or tar at the nozzle. A sample of this was given to the TPW team. Appendix D lists the burner cleaning history.

On-line gas monitoring data was obtained during all tests. Some problems were encountered with the analyzer system. These were corrected as they occurred and the system functioned well under the confined and harsh shipboard environment encountered at sea. Sampling system malfunctions precluded obtaining sufficient samples for organic analysis during the initial three tests (see Section 1.4 for detailed discussions of the problems encountered during the sampling and monitoring activities). These problems were corrected and three subsequent waste burn sampling tests were conducted. The duration of these sampling tests was typically 2-1/2 hours each. In addition, a background sampling test (with the incinerator burning fuel oil) was also successfully accomplished.

Test I - First Waste Test: Problems were encountered at the initiation of the test. The large impinger designed to hold the caustic scrubbing solution collapsed and forced the test to be terminated after 35 minutes. Just before the test was terminated, the quartz liner in the sampling probe cracked due to a temporary thermal overload and a new probe was installed for Test II.

Test II - Second Waste Test: This test was terminated after approximately 20 minutes because the smaller glass impingers (substituted after the Test I problem) that were filled with caustic solution became plugged with a white carbonate precipitate. The thermal overload of the probe, experienced during Test I, was avoided during this test by careful control of cooling flow rates.

Test III - Third Waste Test: The concentration of caustic solution in the impingers was reduced for this test to prevent the formation of the carbonate precipitate, and the test ran smoothly for slightly more than one hour. However, the test then had to be terminated because of a large quantity of sorbent trap resin had passed through a hole corroded in the resin support screen.

Test IV - Fourth Waste Test: This was the first test from which the sample acquired was of sufficient quantity for organic analysis. Sampling was performed for 2.5 hours. During this test, the sorbent trap operating temperature was increased from 25°C to approximately 55°-60°C to reduce the amount of condensation in the sorbent trap module. The caustic solutions and silica gel in the impingers were changed midway through the test. (See Section 3.4.1). One of the starboard incinerator burners (#5) was shut off during the first 20 minutes of the test to repair a valve.

Test V - Fifth Waste Test: Sampling was performed for 2.5 hours. Midway through the test the caustic solution in the impingers was changed. The sorbent module was operated at approximately 70°C. To further reduce the amount of condensation, the sorbent module was run at a slightly higher temperature than the previous test.

Test VI - Sixth Waste Test: Strong wind conditions existed during this test. There was difficulty in keeping the probe stationary and finally it was tied down. About 80 minutes into the test the incinerator was completely shut down for maintenance purposes. The reason for this complete shut down is unknown; however, this was the only such instance where a complete shutdown of one incinerator occurred. Coincident with the shutdown, all three burners were cleaned. During the approximately two-hour delay, the impinger solutions were changed. Total sampling time was 2.5 hours. After the test was over the probe was removed and the liner was solvent washed.

Test VII - Background Test: A baseline test was performed with fuel oil to acquire background data on the performance of the starboard incinerator while burning only auxiliary fuel. A new probe was installed and a three hour sample was procured. About 30 minutes into the test, it was discovered that the incinerator temperature was only about 950°C instead of 1250°C. Operating temperatures were increased to the normal operating temperature by increasing the fuel oil feed rate. The feed rate may have increased too fast because approximately 1.5 hours into the test, flames were observed over the rim of the incinerator. After the test was completed it was impossible to remove the probe from the incinerator. It is believed that when the flames were shooting over the rim of the incinerator the probe became overheated and was bent. After this test was completed the incinerator was shut down. Several hours later, after the probe had cooled, it was possible to withdraw the probe from the incinerator. The probe was then removed and the quartz liner was washed with solvent.

3.2 SAMPLING METHODS

Sampling methods used in the tests were chosen to cover two basic areas:

a) Continuous, on-line monitoring of gas composition to determine and follow steady state conditions.

b) Collection and concentration of effluent gas products to identify and quantify the trace organic species present.

Gas samples for both of these systems were extracted by the same probe. The gases were drawn from the stack area through heat-traced teflon lines and then split. One portion continued on to the portable laboratory installed on the ship which contained the on-line monitoring system. The other portion passed through an organic collection and concentration system.

3.2.1 Probe and Probe Mount

The probe was a stainless steel jacketed, water-cooled probe with a quartz liner and is shown in Figure 3-2. The liner provided an inert surface for the sample gas and the cooled, stainless steel jacket shielded this gas from extreme combustion temperatures in order to quench any further reactions of the sample constituents. Further cooling of the gas was modulated by aspirating an air/water mixture into the space between the steel jacket and quartz liner. The probes were approximately 15 feet in length.

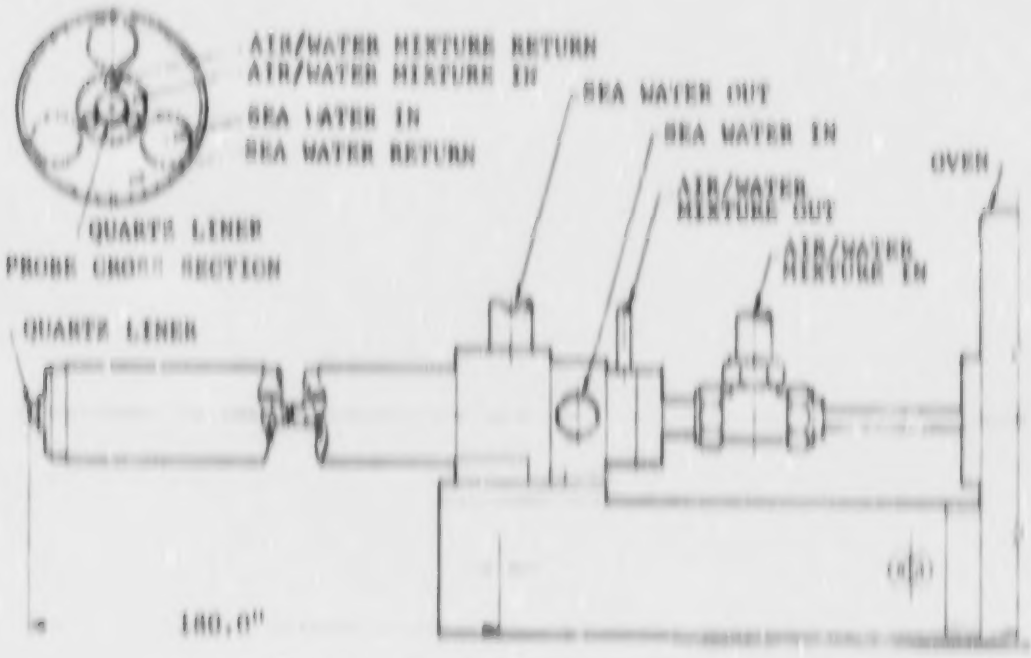

Figure 3-2. Probe design diagram

The probe was supported and moved by the system shown schematically in Figure 3-3 and pictorially in Figure 3-4. Design features for this probe mount are given below:

1. The probe tip was positioned into the effluent gas stream by a pneumatic system. No adjustment was possible for azimuth and elevation.

2. Insertion positioning accuracy was ±0.5 feet by command from the control module which was located on the deck above the bridge.

3. The probe mount was attached to the incinerator flange as shown in Figure 3-5. The outboard end of the mount assembly was supported on an A-frame from the deck.

4. Servicing of the probe required that personnel climb up to the probe mount.

5. Installation of the probe and mount was done in port when no burning was occurring.

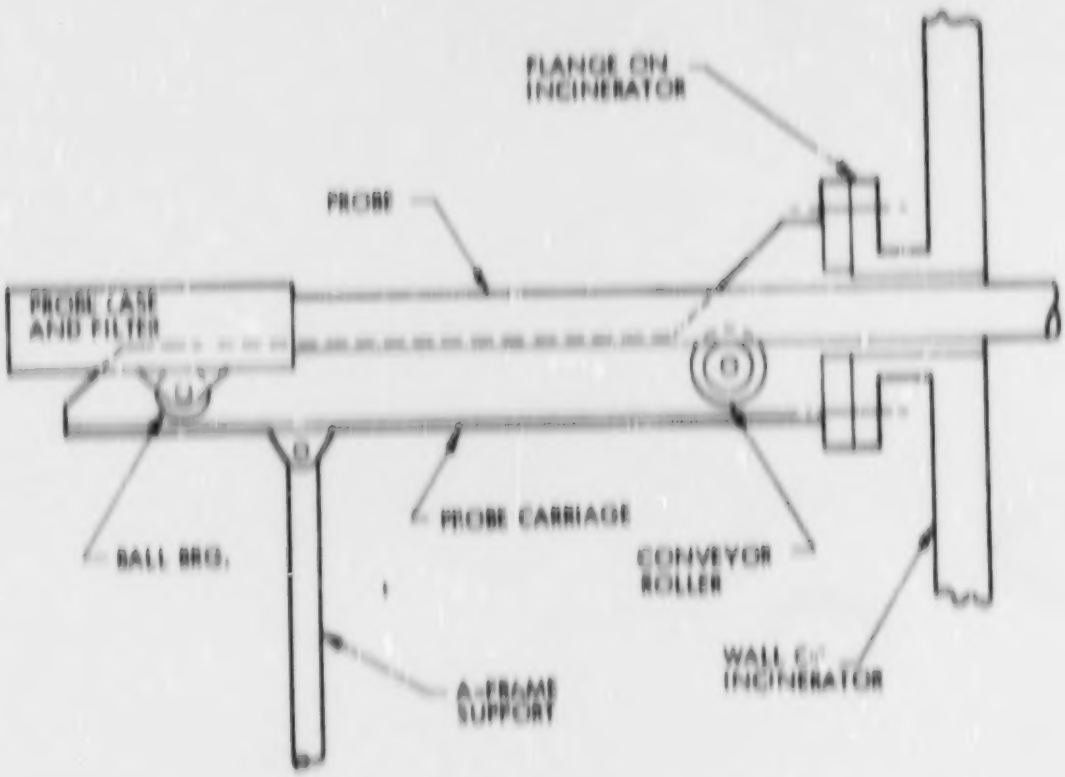

Figure 3-3. Diagram of probe mount for the Vulcanus

Figure 3-4. Probe mount with probe fully withdrawn

6. The following connections were incorporated into the probe or probe mount:

   a) Teflon sample line to connect the probe to the filter housing

   b) Support flanges for the filter oven

   c) Seawater coolant lines for the probe

   d) Air coolant lines for the probe

   e) Thermocouple leads

   f) Pneumatic lines for insertion control of the probe

3.2.2 On-Line Gas Monitoring

A containerized assembly which could be secured on the ship's deck was prepared for monitoring the test burns. A standard fiberglass reinforced plywood (FRP) shipping container was modified to house the on-line monitoring instrumentation and to serve as the portable laboratory for the sampling team. The container previously had been in freight service

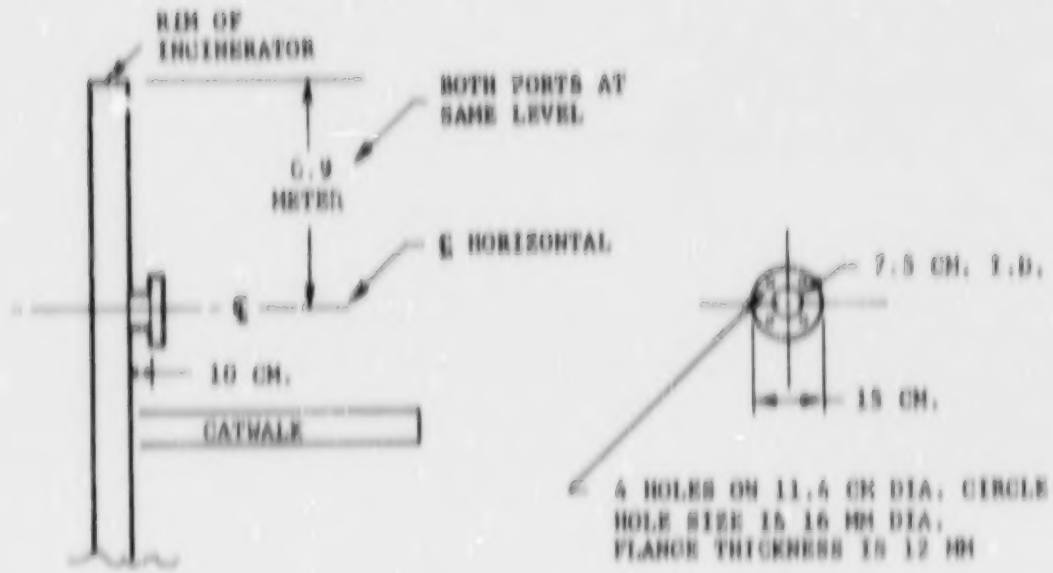

Figure 3-5. Sampling port dimensions

on the Pacific Ocean. Its overall dimensions were 8 x 20 x 8 feet and it was constructed of one-inch plywood with an exterior fiber glass coat. All corners were reinforced with formed and riveted metal members. It was built on a base of approximately 6 inch longitudinal and transverse structural steel channels and beams. A hardwood floor of 2 inch dimensioned lumber was provided and all corners had cast metal stacking and tie-down provisions. One end had a full width double door with heavy hinges, truck type locking mechanism and ample weather stripping. A similar door was provided on one side, but this was permanently blocked by inside structural members. Tare weight was 1850 kg, and maximum gross weight was 20,000 kg. It was estimated that the total weight of the equipment and container was 5,850 kg. The container was lifted or hoisted by slings, and was structurally sound for stacking. It was tied down by using the top corner casting or the base fittings.

The portable laboratory was installed on the starboard side of the deck (Figure 3-6). Because the portable laboratory did not contain an explosion proof electrical system, it could not be placed on the main deck directly above the chemical waste tanks. To comply with U.S. Coast Guard regulations, the portable laboratory had to be over eight feet off the main deck. This was accomplished by placing the portable laboratory on top of a similar container which rested on 12 inch timbers. The

Figure 3-6. Portable laboratory location aboard the M/T Vulcanus

timbers were necessary so that the container would clear a Butterworth hatchcover. The bottom container was used for storage.

The arrangement of equipment in the portable laboratory is shown in Figure 3-7. The on-line gas analyzers were government furnished and are described in Table 3-2. With the exception of the O_2 and CO analyzers, redundant on-line instruments were furnished by EPA. As shown in Figure 3-8, on-line monitoring was performed on the gas sample stream after processing by the gas conditioner. In addition, because the Beckman Model 742 O_2 analyzer would be disabled by HCl vapors, a soda lime scrubber for acid gas was utilized in the oxygen analyzer sample line as shown. A IRW furnished gas chromatograph (Carle Model No. 111) was included in the gas analysis system to serve as a primary back-up for the O_2 analyses and as a secondary back-up for CO_2. This instrument was slated for use only in the event of failure of the primary government furnished analyzers. The continuous on-line monitoring instruments encountered only minor problems which were corrected as they occurred, therefore the gas chromatograph was not needed during the tests.

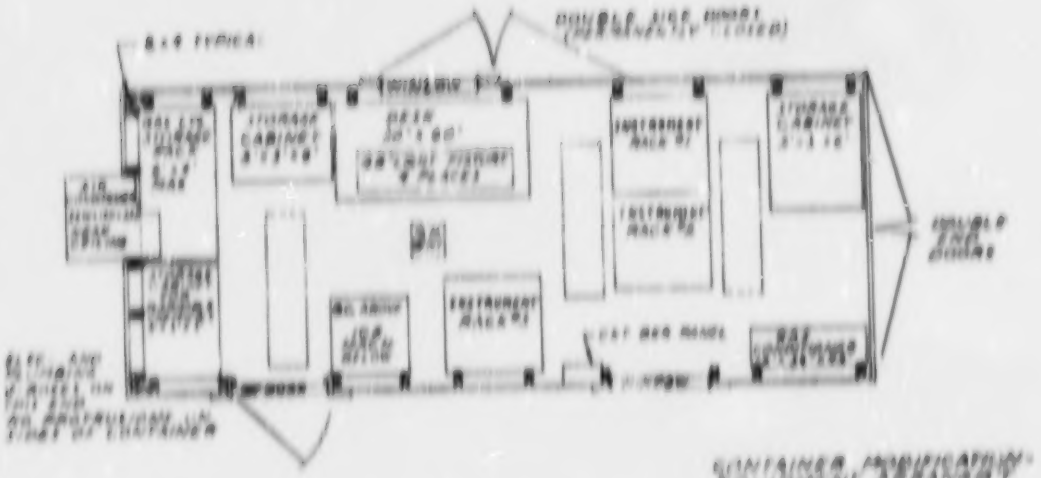

Figure 3-7. Equipment arrangement in the portable laboratory

TABLE 3-2. DESCRIPTION OF ON-LINE INSTRUMENTS

Species Analyzed	Mfg. & Model	Analyzer Type	Instrument Range
Hydrocarbons (HC)	Beckman 108A	FID	0 - 90% in 8 ranges
Carbon Monoxide (CO)	Beckman 315B	IR	0 - 200 ppm, 0 - 2000 ppm, 0 - 2%
Carbon Dioxide (CO_2)	Beckman 315A	IR	0 - 4%, 0 - 8%, 0 - 16%
Nitrogen Oxide (NO)	Beckman 315A	IR	0 - 500 ppm, 0 - 2000 ppm
Nitrogen Dioxide (NO_2)	Beckman 255A	UV	0 - 200 ppm, 0 - 400 ppm
Oxygen (O_2)	Beckman 742	Electro-chemical	0 - 5%, 0 - 10%, 0 - 25%

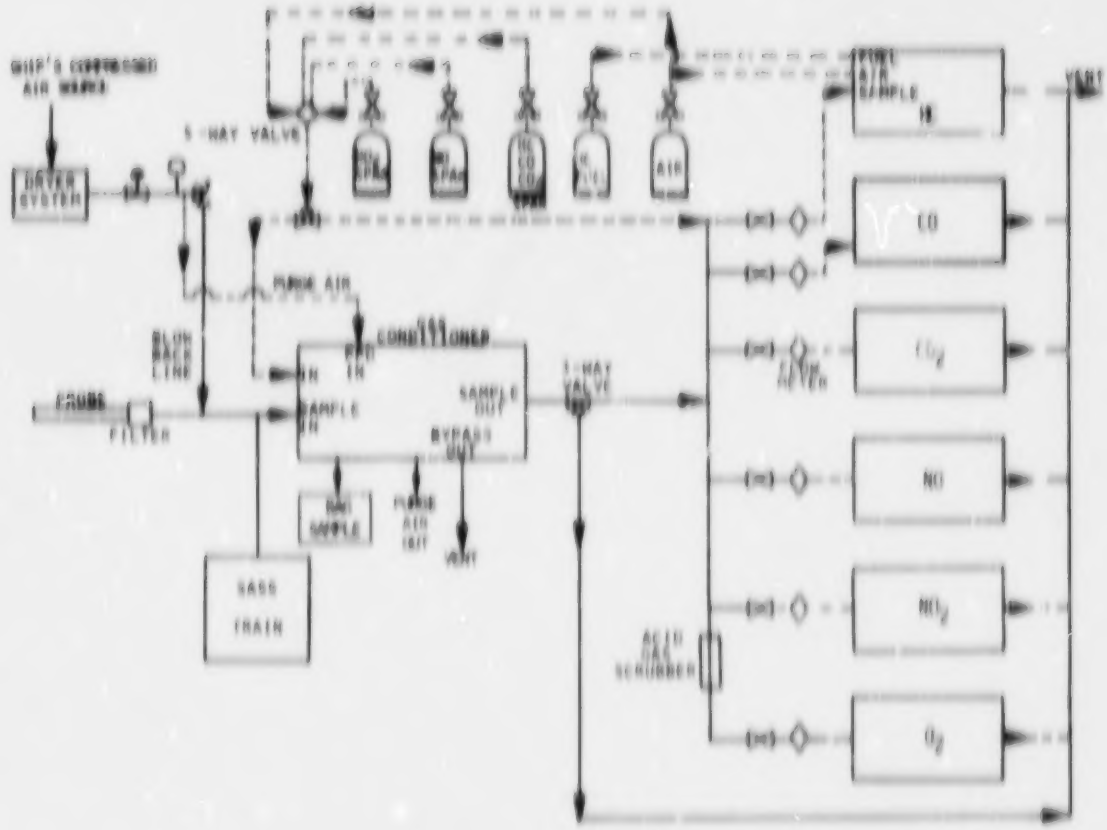

Figure 3-8. Flow diagram of on-line instrument system

3.2.3 Acquisition of Combustion Products

The EPA Source Assessment Sampling System (SASS) was used to trap and remove the organic vapors from the effluent emissions. This high volume sampling train is shown schematically in Figure 3-9. The filter and filter oven associated with the SASS sampling train were mounted on the sampling probe assembly. A heat-traced Teflon line conveyed the sample gases from the filter to the solid sorbent trap module. The sorbent module along with rest of the sampling train was located on the deck above the bridge. This sorbent module, located upstream of the impingers, contained a bed of XAD-2 resin to trap the organic constituents. The module that houses the sorbent trap is temperature controlled to deliver a gas stream as low as 20°C to the trap.

Because the sorbent material is known to have poor trapping efficiency for low molecular, high volatility organic species in the C_1 to C_6 range (Reference 5), it was necessary to supplement the organic sorbent trap. An integrated, composite grab gas sample was taken, therefore, utilizing 20-liter Tedlar gas sample bags. This composite gas sample was taken at

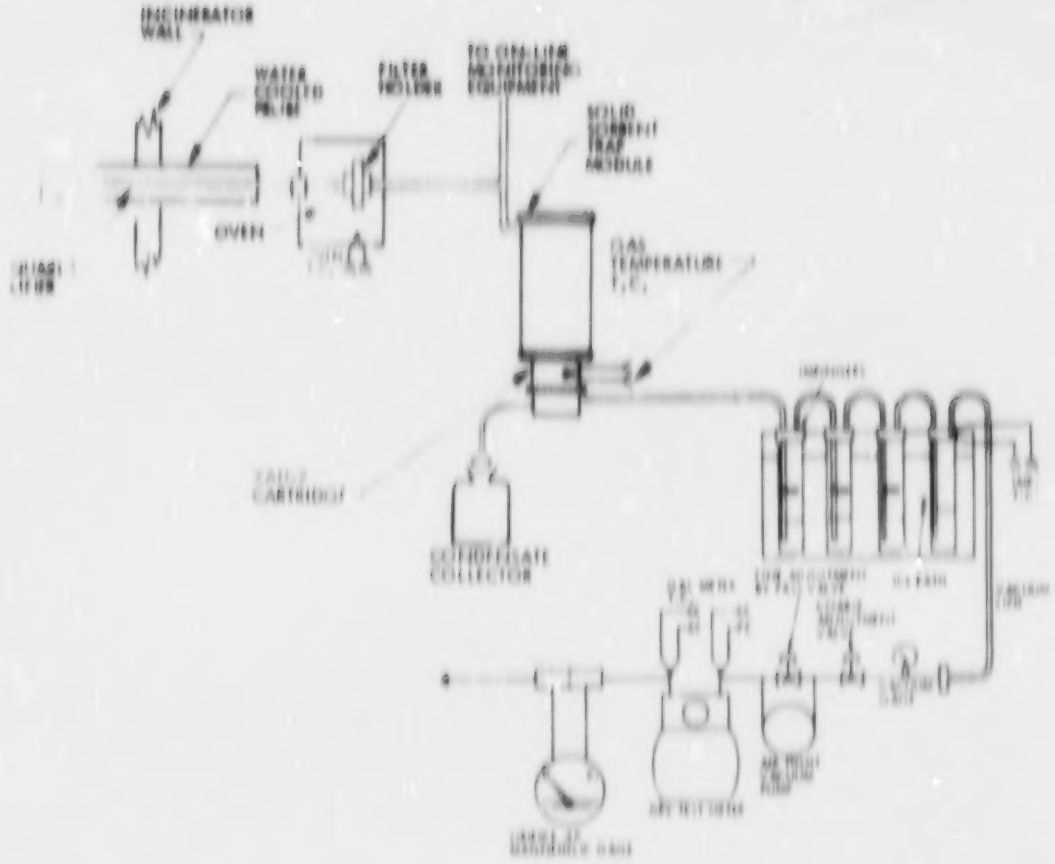

Figure 1-9. Source assessment sampling system (SASS) schematic

the Beckman instrument gas conditioner, which minimized sample alteration and facilitated the sampling operation.

The sampling train was operated at a flow rate of approximately 0.085 cubic meters per minute (cu m/min). Gas volumes were measured to 0.03 liters, with a leak rate of less than 0.1 liters/min. The following samples were obtained from three waste tests and the background test:

- Particulate filter: The filters used in Tests I, II, III and VII were removed from the filter housing with little or no difficulty. The filters from Tests IV, V, and VI, however, were stuck to the perforated metal filter support and broke apart under the slightest attempt to remove them. A metal spatula was used to scrape adhering filter material off the support, but it was not possible to recover it all. The filters were placed in petri dishes for storage and shipment.

- Solvent heated line wash: A pentane rinse of the heat traced line connecting the filter housing and the sorbent trap module was made after each test. The rinsate was collected in an amber glass bottle with a Teflon-lined lid.

- Solid sorbent trap: The canisters were removed from the module and placed in glass jars.

- Sorbent module washes: Departures from the original test plan were implemented on board the ship for the sorbent module trap washing procedure due to the condition of the module after the tests. The surfaces contacting the sample gas were coated with a mixture of what appeared to be metal chloride salts, HCl and water. The original washing sequence of pentane/methylene chloride, isopropyl alcohol and pentane was ineffective in removing the surface coatings. A field decision was made to use rinse solvents in the following order 1) water (which dissolved the salt coating), 2) isopropyl alcohol, 3) pentane/methylene chloride, and 4) pentane. All washings were placed in amber glass bottles with Teflon-lined lids. The sorbent module from Test VII (fuel oil background) was disassembled after the test and an attempt was made to clean it. It was coated with a heavy layer of what appeared to be iron rust. These deposits were not removable with any of the available solvents aboard ship. The entire module assembly was packed up and shipped back to the laboratory for further inspection and solvent rinsing.

- Condensate solution: The condensates from the sorbent trap module were transferred to amber glass bottles with Teflon-lined caps.

- Combined impinger solutions: The caustic impingers were combined and stored in amber glass bottles with Teflon-lined caps.

- Acidified split of combined liquid impingers: An aliquot of each impinger sample was transferred to a Nalgene bottle and acidified with nitric acid.

- Spent silical gel: The spent silica gel was stored in glass bottles.

- Three grab gas samples: The Tedlar bags were packed in sturdy fiber drums.

Solvent washes of the quartz liner were not performed after each waste burn test due to the delicate and hazardous nature of the operation. The probe used for tests II through VI was rinsed with pentane after it was removed. A rinse of the Test VII (background) probe was also made. Pentane was poured into the quartz liner inlet using a funnel and was collected from the outlet in an amber glass bottle fitted with a Teflon-lined cap. The inclined probe was rotated to insure solvent contact with all interior surfaces of the quartz liner.

3.3 ANALYSIS TECHNIQUES

Samples taken as described in Section 3.2 were analyzed for both organic and selected inorganic constituents. The techniques used for the various sample preparation steps are described below, and the analysis methods are described in the subsequent section.

3.3.1 Extractions and Sample Preparation

Samples were removed from the sampling train, stored and prepared for analysis as described below by sample type.

Probe Washes: In the laboratory the probe wash samples were inspected for suspended solids and, seeing none, they were dried over anhydrous sodium sulfate. These samples were then measured for volume, a small aliquot was taken, and the remainder was concentrated down to 10 ml to be analyzed for organic materials including waste constituents.

Filters: The filters were not weighed because the 1) loss of filter material and 2) substantial amounts of crystalline corrosion products on the filters, precluded any accurate determination of particulate weight. Thus particulate mass loadings could not be determined for these tests. The filters were, however, extracted for organics with pentane for 24 hours. The pentane extracts were dried over anhydrous sodium sulfate, diluted to volume and an aliquot was taken for storage. The remainder was concentrated down to 10 ml.

Heated Line Washes: During laboratory preparation this rinse was combined with the pentane extracts of the sorbent trap resin into one sample.

Sorbent Canisters: Changes in the procedures for extracting and preparing the contents of the sorbent canisters for analysis were implemented due to the extensive coating of the resin with corrosion products. It was found that pentane, the planned first solvent for extraction, had no apparent effect on their removal. Water was found to have good dissolving power, and it was decided to extract the resin and rinse the canisters first with water. The canisters were soaked in deionized water to dissolve the deposits on them, and the resulting liquid was added to the water used to make the first resin extraction. This aqueous Soxhlet extraction of the resin was carried out for four hours. The resin samples in the thimbles were drained of as much water as possible, and the water extracts were in turn extracted with pentane using separatory funnels.

Pentane was added to the Soxhlet extractors to continue the extraction after the water extract was removed. However, the immiscibility

of the pentane with the remaining water in the resin would not permit wetting of the XAD-2 with the pentane. In addition, the pressure caused by the pentane column height was not sufficient to force the water through the siphon tube and cause the extractor to "dump". To correct this situation, 50 milliliters of acetone (nanograde) was added to each thimble. The acetone mixed with the water and purged the water from the resin. These acetone/water rinses were transferred directly into the Soxhlet receiving flask, along with the pentane required for the next extraction step. The pentane resin extraction was then carried out for 24 hours.

The pentane extracts of the resin samples were combined with two other pentane samples: 1) the pentane rinse of the heated lines, and 2) the pentane extract of the water used to extract the XAD-2 resin. The combined solutions were dried over sodium sulfate, an aliquot was taken for archival storage and the remainder was concentrated down to 10 ml for organic analysis.

Sorbent Module Washes: The laboratory preparation procedures for these samples were as follows:

a) The water washings were liquid/liquid extracted with pentane using a separatory funnel. The pentane layer was saved for combination with other washings of the module.

b) The IPA washings were dried over anhydrous sodium sulfate and concentrated down to 10 ml.

c) The pentane/methylene chloride and neat pentane rinsings were combined with the pentane extract of the module water wash (item a). This solution was dried over sodium sulfate and then concentrated down to 10 ml for organic analysis.

The uncleaned module from test VII was photographed and washed sequentially with IPA, 50/50 pentane/methylene chloride solution, and finally pentane. The rust coating remained after the rinsings. The rinses of the test VII module were treated the same as the other test samples.

Sorbent Module Condensates: In the laboratory, the condensates were neutralized to pH 7 with sodium hydroxide, and then extracted with pentane in separatory funnels. The pentane extracts were dried over anhydrous sodium sulfate and concentrated to 10 ml.

Impinger Solutions: No preparation or analyses were performed on either the neat impinger solutions or the acidified splits of these samples. These samples would normally be analyzed for inorganic constituents, however, inorganic analysis was not required for this program.

Silica Gel: The spent silica gel was reweighed in the laboratory to determine the amount of water absorbed. The silica gel was then regenerated for future use.

Grab Gas Samples: No preparation was required for these samples.

3.3.2 Analysis of Concentrated Extracts

The organic samples, in the form of 10 ml concentrates, were analyzed by a combination of qualitative and quantitative techniques. The qualitative techniques were selected to generally characterize the major organic components in the concentrated samples, and the quantitative techniques focused on the waste constituents and hazardous potential by-products.

Gravimetry: Aliquots (1-2 ml) of the 10 ml concentrates were evaporated in small glass bottles at ambient conditions to remove the solvent. The residues were weighed on a micro-balance.

Infrared Spectrometry (IR): The organic residues obtained in the gravimetric determination were examined by IR on a Perkin Elmer Model 521 Grating Spectrophotometer. When there was sufficient material, the sample was run as a smear on a salt window. Smaller quantities were mixed with KBr and pressed into a pellet for analysis.

Low Resolution Mass Spectrometry (LRMS): Microgram quantities of the sample residue were transferred to a glass probe tip which was, in turn, placed in the batch inlet probe of a Hitachi RMU 6 magnetic sector mass spectrometer. The probe tip was ballistically heated from 50° to over 400°C and a mass spectrum was taken every 60°C.

Gas Chromatography/Mass Spectrometry (GC/MS): Two instrument systems were used for this portion of the analysis. System 1 was a Finnigan 9500 gas chromatograph interfaced via a single stage glass jet separator to a Finnigan model 11000 quadrupole mass spectrometer controlled by a System Industries, System 250 computer software package. System 2 was a Finnigan 9610 gas chromatograph interfaced via a glass jet separator to a Finnigan model 4000 quadrupole mass spectrometer. This system is controlled by a Data General Nova 3 computer and a Finnigan-Incos software package. The scan cycles and mass ranges varied somewhat between systems, but scan cycles were typically 1.8 to 2.0 sec. Mass ranges were typically between 20 and 300, but were expanded out to as much as 600 mass units as required.

The GC column in System 1, used for all the samples, was 3 percent OV-17 on 100/120 mesh Chromosorb W AW-DMCS. The oven was programmed from 20°C to 200°C at 12°C per minute. Repeat analysis for confirmation of original data and more details was performed using GC/MS System 2. Slightly different column lengths and program rates were used to achieve similar retention times with the two instruments. A Chromosorb 101

column was subsequently used on a limited number of samples where the initial data indicated that light volatile materials required better separation. The oven was programmed from 125°C to 225°C at 10°C per minute.

3.3.3 Analysis of Gas Bag Samples

Although some degradation of the Tedlar bags' nylon fittings had been observed (see Section 3.4.6), no damage critical to sample integrity was noticed upon packing the bags for shipment to TRW's Redondo Beach, California facility nor when they were inspected after arrival. Soon after their arrival at TRW, the gas bag contents were analyzed directly by low resolution mass spectrometry (LRMS). For improved sensitivity, a subsequent analysis was planned using a pre-concentration on Tenax/GC followed by gas chromatography analysis. In the interim between the LRMS analysis and Tenax/GC analysis, however, the fittings cracked and degraded. The fitting literally fell to pieces. The bags were resealed with tape and a new fitting was installed in each damaged bag. The contents of the bag for each test were transferred to new bags and the Tenax/GC work started immediately.

Tenax/GC, a porous polymer GC column packing material, was used to concentrate the trace organic materials in the bag samples. Liter quantities of gas from the bags were passed through columns packed with Tenax. The Tenax columns were then thermally desorbed and the desorbed species analyzed by gas chromatography with flame ionization detection (FID).

3.4 PROBLEMS ENCOUNTERED

In spite of detailed planning and preparation for these field tests, a few incidents occurred that had not been anticipated. The main factors contributing towards these incidents were the initial sampling operations on a shipboard incineration program by the sampling team and several components of the sampling system which were comparatively new technical developments with very little field experience. The problems which occurred during the sampling and monitoring activities on board the Vulcanus are described in the following paragraphs.

3.4.1 Sampling Train Impingers

Sodium hydroxide was added to the sampling train impingers to scrub out the hydrochloric acid (HCl) thereby protecting the pumps and dry test meter. The high volume sampling train used in these tests as well as the high concentration of HCl in the effluent gases (approximately 6 percent), required a large amount of sodium hydroxide. In order to accommodate the sodium hydroxide the sampling train was altered to include a two gallon polypropylene bottle containing sodium hydroxide which was installed in the sampling system between the sorbent module and the impinger system. Once the first test was initiated the vacuum created in the sampling system by the pumps slowly collapsed the bottle

thereby forcing the solution into the regular impingers. This problem was solved by substituting additional glass impingers for the polypropylene bottle.

Before the main problem was diagnosed in the first test, it was noted that the sampling flow rate was only 0.03 cu m/min. As a consequence of this low flow rate, the sample gas coming out of the probe couldn't be maintained above 120°C. In trying to increase the temperature of this gas, inadvertently the probe became overheated and the resulting deformation caused the quartz liner to crack. This necessitated changing the probe before the second test was initiated.

Fifteen minutes into the second waste test the sample gas flow rate dropped off and finally stopped. The impingers containing the sodium hydroxide solution were caked with a thick white precipitate. The carbon dioxide in the effluent gases had reacted with the concentrated sodium hydroxide solution to form insoluble carbonate salts. The original concept had been to use a concentrated sodium hydroxide solution (50 percent) so that the impinger solutions would not have to be changed during the test. To minimize the precipitate problem the caustic solutions were diluted to 10 percent solutions and were changed during the tests. When HCl vapors were detected in the control module exhaust (using litmus paper), the sampling train operation was stopped so that the caustic solutions could be changed. When the caustic solutions were changed, the last impinger containing the silica gel was also changed. The silica gel was used to protect the pumps and dry test meter by removing the moisture from the gas stream.

3.4.2 Sorbent Module

The major problems encountered with the operation of the SASS train were due to the hostile operating environment. Because the waste was highly chlorinated (50-70 wt percent halogen as chlorine), the operating conditions of the incinerators produced an effluent gas which contained approximately 6 percent hydrogen chloride (HCl). It was also noted that during the sampling tests the relative humidity was high (~50 percent) thereby adding to the moisture content of the effluent gas. Any condensation of the effluent gas produced a very corrosive environment. The SASS train, with all its stainless steel components simply was not designed to operate under these corrosive conditions.

The main problem with the sampling system was corrosion in the sorbent module. This was first noted in Test III. When the condensate was first emptied into the drain bottle, there was an appreciable amount of liquid of a dark green color. The problem actually surfaced about one hour into the test when a large amount of resin was detected in the drain bottle after one of the periodic emptyings of the condensate reservoir section. The resin had ended up in the drain bottle because the acidic environment had corroded a hole in the stainless steel screen supporting the resin and a considerable portion of the resin had dropped into the condensate collection section. Other observations revealed

that the whole module was heavily coated with corrosion products. Several solvents were used to try to remove these corrosion products, however, distilled water proved most successful.

Originally the sorbent module was intended to be operated at 20°C, i.e., the effluent gas entering the XAD-2 resin would be at this temperature. During Test III the module had been operated at 25°C. This was the lowest temperature that could be obtained. Because of the corrosion caused by the large amount of condensation at that temperature, for the remainder of the sampling tests it was decided to operate the sorbent module at a higher temperature (55-70°C) in order to try to reduce or minimize condensation in the module. This seemed to reduce the amount of condensate which was collected in the drain bottle; however, the module was still heavily coated with corrosion salts. Operating the module at these higher temperatures allowed the train to be operated long enough to collect a sufficient sample for organic analysis.

3.4.3 Filter Holder

In all the sampling tests which involved waste burning, there was a problem in trying to remove the filter from the holder. The filter was stuck to the support screen and could not be removed in one piece. In several instances the filter had to be scraped off the screen. There was also evidence of corrosion on both the screen and filter holder. This problem was not encountered during the background sampling test when the incinerator was operated on only fuel oil.

3.4.4 SASS Train Control Unit

The control unit worked very smoothly until the last day of testing. During the background test (fuel oil) the thermocouple readings became very erratic. A hand-held temperature readout device (API Instrument Co.) was used to check the thermocouples. The results indicated that the thermocouples were functioning properly, therefore, for the remainder of the test the API Instrument was used to obtain the thermocouple readings.

3.4.5 On-Line Instrumentation

A progressive deterioration of performance, i.e., base-line drift, was noted with the CO_2 analyzer. Frequent calibration of the analyzer was required in order to obtain reliable data. The instrument tended to stabilize; i.e., return to levels of prior performance, during the final, background test when there was no HCl persent. The NO analyzer caused some difficulties, especially when trying to "zero" the instrument, but that anomaly disappeared after one day. There appears to have been no day-to-day effect of HCl on the oxygen analyzer (semipermeable membrane) or the hydrocarbon analyzer (flame ionization detector). The oxygen analyzer had a soda lime scrubber to remove HCl which was effective.

After observing the daily operation and performance of the instruments as the test program progressed, there were indications that HCl in the combustion gas may have been the source of drift and noise problems. The manufacturers of the non-dispersive infrared analyzers (CO, CO_2, and NO) claim that no significant damage will occur to the materials of construction if the sample containing the HCl is moisture free. In the initial test, when the quartz liner cracked, a moisture laden sample reached the on-line monitoring system. Before any further tests were performed, the complete on-line analyzer system was thoroughly cleaned and purged with air. Before the background test was started, the analyzer system was again thoroughly cleaned and purged with air. During this cleaning, moisture was very much in evidence throughout the system.

3.4.6 Degradation of Gas Bag Fittings

During the sampling program at sea, it was noticed that the internal parts of the nylon fittings were beginning to soften or melt as evidenced by a loss of definition in sharp corners and machined threads, etc. It is believed that HCl in the combustion gases hydrolytically attached to the nylon to cause polymer chain scission and physical failure of the part. No damage was observed on the gas bags for the fuel oil background run where HCl was not present. The fittings were inspected each day, and it appeared that the attack seemed to stop before the fitting leaked or could not function.

4. TEST RESULTS

Six sample tests and one background test were run. The test results described in the following sections include:

- Data taken in the field during the tests.
- Data from analysis of the test samples in the laboratory.

4.1 OPERATIONAL AND FIELD DATA SUMMARY

Data acquired on board the ship during the tests covered the subjects of waste feed rates, temperatures in the incinerators, on-line gas composition monitoring, plume characteristics, and ambient HCl levels on the ship's decks. Each of these are discussed in the following sections.

4.1.1 Waste Feed Rate and Mass Emissions

Time averaged waste feed rates were recorded during the burn period. These data are shown in Table 4-1. The time and tank volume data were provided by the M/T Vulcanus and are contained in Appendix A. Total incineration time for the waste was 186 hours and 45 minutes during which time 4100 tonnes of waste were burned. The average waste feed rate was thus approximately 22 tonnes/hr. This rate is based on the time required to deplete each tank and on a depth sounding at the start and end of drawing waste from the tank.

The theoretical emission rates of the major stack gas components from each furnace were calculated. Based on an average waste feed of 11 tonnes/hr, the elemental composition of the waste, an average excess air of 90 percent, and a relative humidity of 80 percent at 29.4°C (85°F). The resulting values were:

		Mole Percent in Stack Gas	
Species	Emission Rate	Wet Basis	Dry Basis
CO_2	6,160 Nm^3/hr	8.20	8.82
HCl	4,350 Nm^3/hr	5.79	6.23
H_2O	5,280 Nm^3/hr	7.03	-
O_2	6,630 Nm^3/hr	8.83	9.49
N_2	52,690 Nm^3/hr	70.15	75.45

for a total stack gas emission rate of 75,110 normal cubic meters (at 0°C) per hour (Nm^3/hr). The calculations were based on the assumptions that the chlorine present in the waste was converted to HCl, the carbon was converted to CO_2, and the hydrogen was converted to HCl and H_2O. These assumptions have been verified by both thermodynamic equilibrium calculations and actual measurements, which indicated that HCl was the predominant chlorine compound present and that CO was present only at ppm levels in the stack gas. Of the water vapor emitted with the stack gas, approximately 45 percent (2,360 Nm^3/hr) was due to the presence of moisture in the inlet air. Also,

TABLE 4-1. WASTE FEED RATES

Tank Number	Volume (cu m)	Start Day	Start Hour	End Day	End Hour	Time (cu m)	Volume Burned (hrs)	Feed Rate (T/hr)[a]
2C	562	3/5	2000	3/7	0400	32	556	22.5
5C	415	3/7	0400	3/8	0300	23	383	22.0
1	444	3/8	0300	3/9	0530	26.5	440	21.5
4C	425	3/9	0530	3/10	0515	23.75	396	21.5
3C	398	3/10	0515	3/11	0500	23.75	406	22
2P	256	3/11	0500	3/11	1815	13.25	243	24
3P	232	3/11	1815	3/12	0715	13	221	22
4P	300	3/12	0715	3/13	0215	19	300	20.5
5P	234	3/13	0215	3/13	1415	12	222	24

a) T = tonne (1000 kg)

at 90 percent excess air, the combustion air feed rate was calculated to be 75,160 m3/hr (wet basis at 25°C), or about 16.5 percent below the maximum combustion air feed rate of 90,000 m3/hr.

4.1.2 Temperature and Residence Time

Direct flame temperatures were measured in the furnaces using a Leeds and Northrup Optical Pyrometer, Catalog No. 8621, Serial No. 1009965. Calibration of this instrument was furnished in a notarized document from Leeds and Northrup, Houston, Texas, in February, 1977. This instrument operates in the 6500 Å region using a 500 Å band-pass. It is probable that the HCl in the combustion products would not have a large effect on the validity of the temperature readings from this instrument because the principal frequency for HCl absorption is 6 microns (60,000 Å). Any effects at the operating frequency of 6500 Å would be due to 6th or 7th overtones which would be relatively very weak.

The data taken by the Chief Engineer of the Vulcanus, comparing the flame temperatures with the thermocouple-derived wall temperatures is contained in Appendix B. This comparison was performed in order to establish a statistical relationship between wall and flame temperatures. The desired result is a correlation between flame and wall temperature such that automatic shut-off of waste to the burners can be triggered from wall temperature, using a preset value on the automatic shut-off system. The controller minimum temperature setting was 1200°C. The controller is neither locked nor sealed and therefore it is possible to alter the temperature setting.

The statistical correlations between flame temperature and controller temperature for the starboard and port incinerators are presented in Figure 4-1 and 4-2 respectively. These graphs also indicate the variations in flame temperature to be expected at a given controller temperature at different confidence levels. For example, to determine the starboard controller temperature to insure that flame temperature will exceed 1300°C at a confidence level of 99.9%, a line is first drawn from 1300°C on the flame temperature axis horizontally to intersect the lower 99.9% confidence level line. Next, from this intersection, a vertical line is drawn downward to the controller temperature axis, where a value of 1180°C is obtained. This means that if the controller temperature is 1180°C, there is a 99.9% probability that the flame temperature is 1300°C or higher. Conversely, there would be only 1 chance in 1000 that the flame temperature would be less than 1300°C if the controller temperature was 1180°C.

Figure 4-2 can be used in a similar manner to determine the relationship between flame temperature and controller temperature for the port incinerator. This technique can be used both to select a given set of flame/controller temperatures for setting the automatic waste shut-off system and to estimate the probability of having attained adequate flame temperatures given the controller set temperature.

The residence time of combustion gas in the furnace can be calculated from the stack gas emission rate (discussed in Section 4.1.1) and the furnace volume. Since the volume of each furnace is 120 m^3, the residence time, t, for each furnace can be calculated as:

$$t = \frac{120}{\frac{75,110}{3,600} * \frac{T}{273.16}} \quad sec$$

where T is the furnace temperature in °K. The residence times calculated are given below:

Flame Temperature (°C)	Residence Time (sec)
1100	1.14
1200	1.07
1300	1.00
1400	0.94
1500	0.89
1600	0.84
1700	0.80

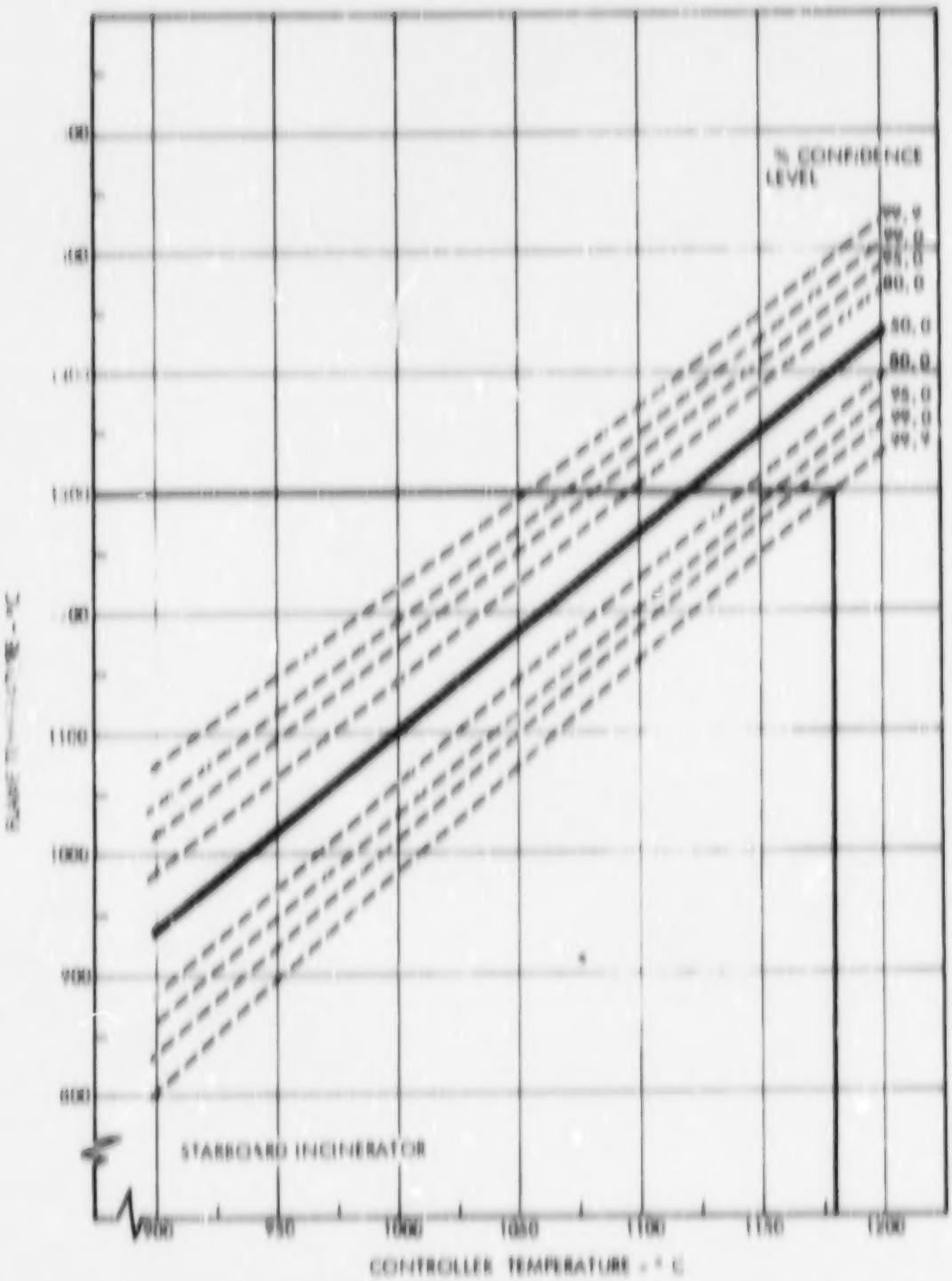

Figure 4-1. Controller/flame temperature correlation - starboard incinerator.

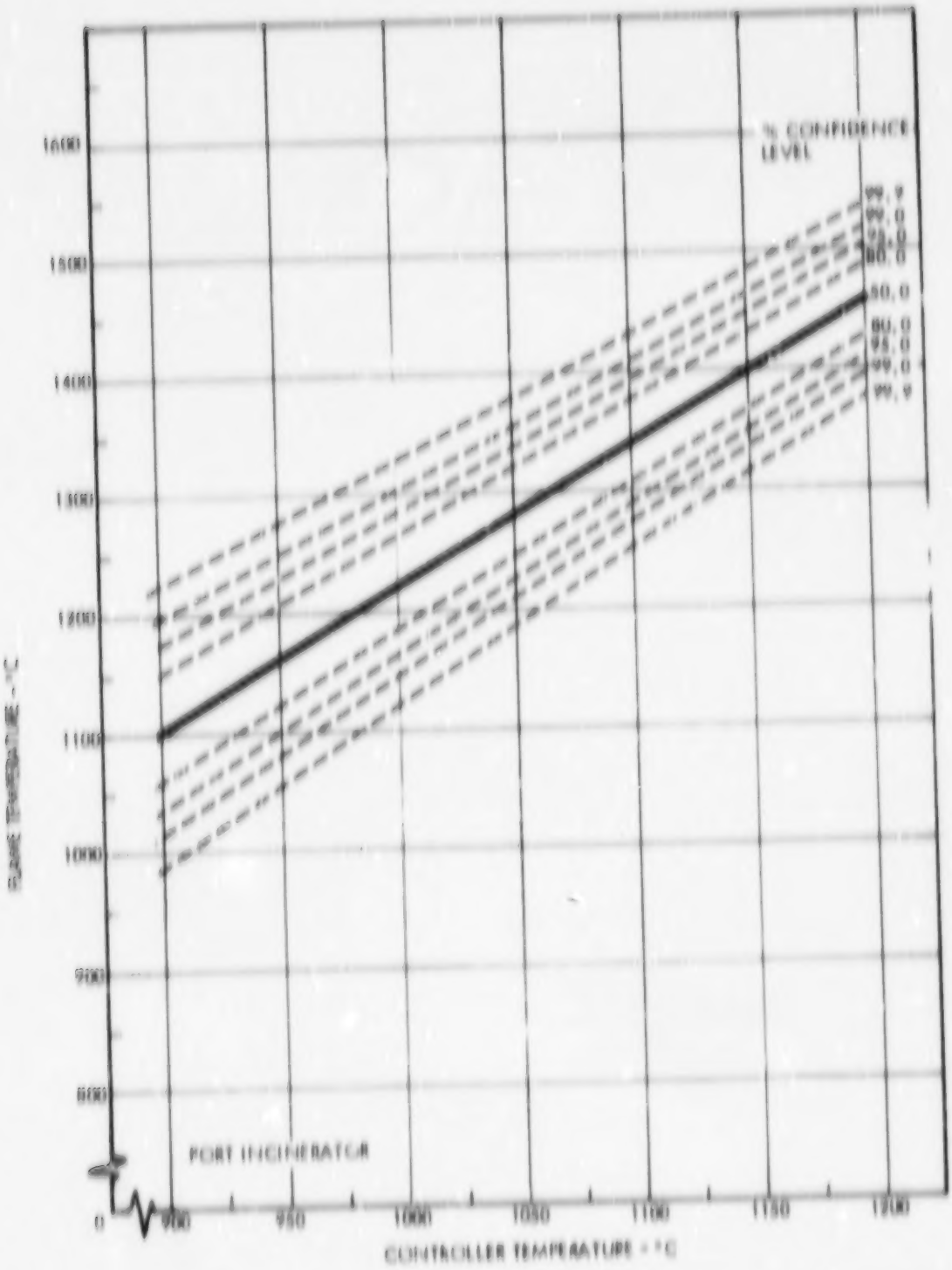

Figure 4-2. Controller/flame temperature correlation - port incinerator.

4.1.3 On-Line Gas Composition

Signal outputs from the on-line instruments were recorded on strip charts and an Esterline-Angus data logging device which automatically printed out the millivolt signal from each instrument at two minute intervals. Data was recorded during the duration of the operation of the SASS train. The monitoring was interrupted only when 1) the SASS train was shut down or 2) instrument calibration checks were made during a test.

The results of the gas composition analyses, presented in Table 4-2, were calculated on a dry basis, i.e., the samples were water free when analyzed and no correction has been made for removed moisture. The oxygen values have been corrected for the volumes of CO_2 and HCl which were removed from the oxygen analyzer sample feed before analysis. The range of levels for each species shows the maximum and minimum levels seen for all valid data points. The average value is a numerical average of all valid points.

The strip chart recordings of the on-line instruments were compared to logged sampling and monitoring events occurring during the run. When a transient condition was observed on a recording (an unusually high or low short term datum point inconsistent with surrounding data) which correlated in time with a logged, physically observed occurrence, a review was made of the probable association between the events. Data was only considered nonrepresentative of the incineration process when it was highly probable that an unrelated event, such as turning on of the sampling pump, etc., caused the apparently spurious result.

A few transient data points occurred each time the sampling system was started, since material that had condensed in the probe before sampling was then vaporized and pulled into the gas composition analyzers. This particularly affected the hydrocarbon and CO analyzers, which read ppm levels. Transient "spikes" of CO and hydrocarbons on the strip chart during start of sampling were therefore not included as representative data points. Erratic data near the end of Test I were also eliminated, because these points occurred after the probe liner had broken and cooling water entered the sampling system. A transient "spike" in CO and hydrocarbon data during Test IV was observed when burner #5 was restarted after replacement of a valve associated with the #5 burner. Performance of the incinerator was improved after this maintenance was completed, as indicated by an increase in CO_2 and decrease in CO measurements. Both performance levels were included in the Test IV data; however, the transient data during burner restart was deleted. The wide range of gas composition data and combustion performance during Test VII, the background test with fuel oil, resulted because feed rates were varied during the test to increase temperatures to levels more comparable to the waste tests.

TABLE 4-2. GAS COMPOSITION DATA SUMMARY

Test No.		O_2 (Percent)	CO_2 (Percent)	CO (ppm)	HC (ppm)	HC[a] (ppm)	HC[b] (Percent)	N_2[c] (Percent)	Destruction[d] efficiency	Excess Air[e] (Percent)
I	Range	10.5–12.4	7.4–9.8	17–35	35–148	35–74			99.95–99.99	
	Average	11.7	8.8	27	97	53	6.2	72.3	99.97	150
II	Range	8.2–8.7	11.4–11.9	25–39	90–128	42–69			99.95–99.98	
	Average	8.5	11.7	36	98	55	8.1	71.5	99.97	85
III	Range	8.3–10.6	10.5–11.5	28–33	69–94	9–16			99.97–99.98	
	Average	8.8	11.1	29	80	10	8.0	71.8	99.97	90
IV	Range	6.5–15.7	5.9–12.1	3–42	8–163	3–36			99.94–99.99	
	Average	11.1	8.2	13	58	19	6.5	73.2	99.96	135
V	Range	4.3–13.6	5.1–7.3	6–47	10–1588	1–10			99.92–99.98	
	Average	11.4	5.9	17	134	7	4.2	78.6	99.97	105
VI	Range	5.5–9.7	7.6–11.4	3–78	75–187	2–20			99.96–99.99	
	Average	8.2	9.6	40	75	9	6.8	75.4	99.96	70
VII[f]	Range	1.8–13.4	4.9–12.7	3–76	8–1076	0–76			99.91–99.99	
	Average	7.4	9.5	28	306	7	6.7	76.4	99.97	60

[a] As methane

[b] Calculated as a ratio to CO_2 based on 36.0% carbon and 52.6% chlorine in the waste feed

[c] By difference

[d] $\frac{[In]_i - [In]_f}{[In]_i} \times 100$

[e] See Section 3

[f] Background test (fuel oil)

The combustion efficiency is calculated from the CO_2 and CO concentrations of the effluent gases using the following equation:

$$\% \text{ Combustion Efficiency} = \frac{[CO_2] - [CO]}{[CO_2]} \times 100$$

Based on the data obtained during the monitoring of the M/T Vulcanus, the average combustion efficiencies for each run ranged from 99.96 to 99.98 (Table 4-3).

EPA Method 3 was used to calculate the excess air in the effluent gases. The following equation is utilized:

$$\% \text{ Excess Air} = \frac{[O_2] - 0.5[CO]}{.264[N_2] - ([O_2] - 0.5[CO])}$$

The excess air ranged from 60 to 150% and, as seen from Table 4-2, the average oxygen concentration ranged from 7.4 to 11.7%.

A summary for each of the gases measured during the test series is provided in Table 4-3. The data entries are based on the two minute readings for each gas over the entire test series. This provides the highest and lowest valid two minute reading observed during any of the tests, the average reading, the standard deviation and the number of valid 2 minute readings used. The tolerance band provides the range in 2 minute readings which will include 99% of the data with a confidence of 90%. That is, if all conditions were exactly the same for the incinerator, feed, etc., in further tests, 99% of the valid data acquired would be found to lie within the range in 90% of the tests made. The tolerance band is based on an assumption of normal population of data.

The data acquired during tests IV, V, and VI provide a large sample for study of incinerator effluent characteristics. These three tests provided data for different days of operation, different tanks of waste, and several different probe positions. The tests were sampled extensively through the water-cooled probe/on-line instrument system, providing data at two minute intervals for all 5 gases (O_2, CO_2, CO, NO, volatile hydrocarbons). The data obtained at the two minute sampling rate was recorded on printed paper tape. This tape was corrected before use in the statistical studies. The correction was made by comparison with the continuous reading strip chart recorders for each instrument, and log books, to remove the data transients identified on the strip charts as occurring after instrument start-ups or probe adjustments. The corrected tape thus provides a data base for a statistical study of probe position effects and time-oriented furnace performance changes. A summary of the data base is provided for each of the gases in Figures 4-3, -4, and -5, for the three tests. Figure 4-6 is a plot of the combustion efficiency versus time for the three tests.

TABLE 4-4. TEST SERIES 1-H1 (Water Tests)

| Test Series 1-H1 (Water Tests) | | |

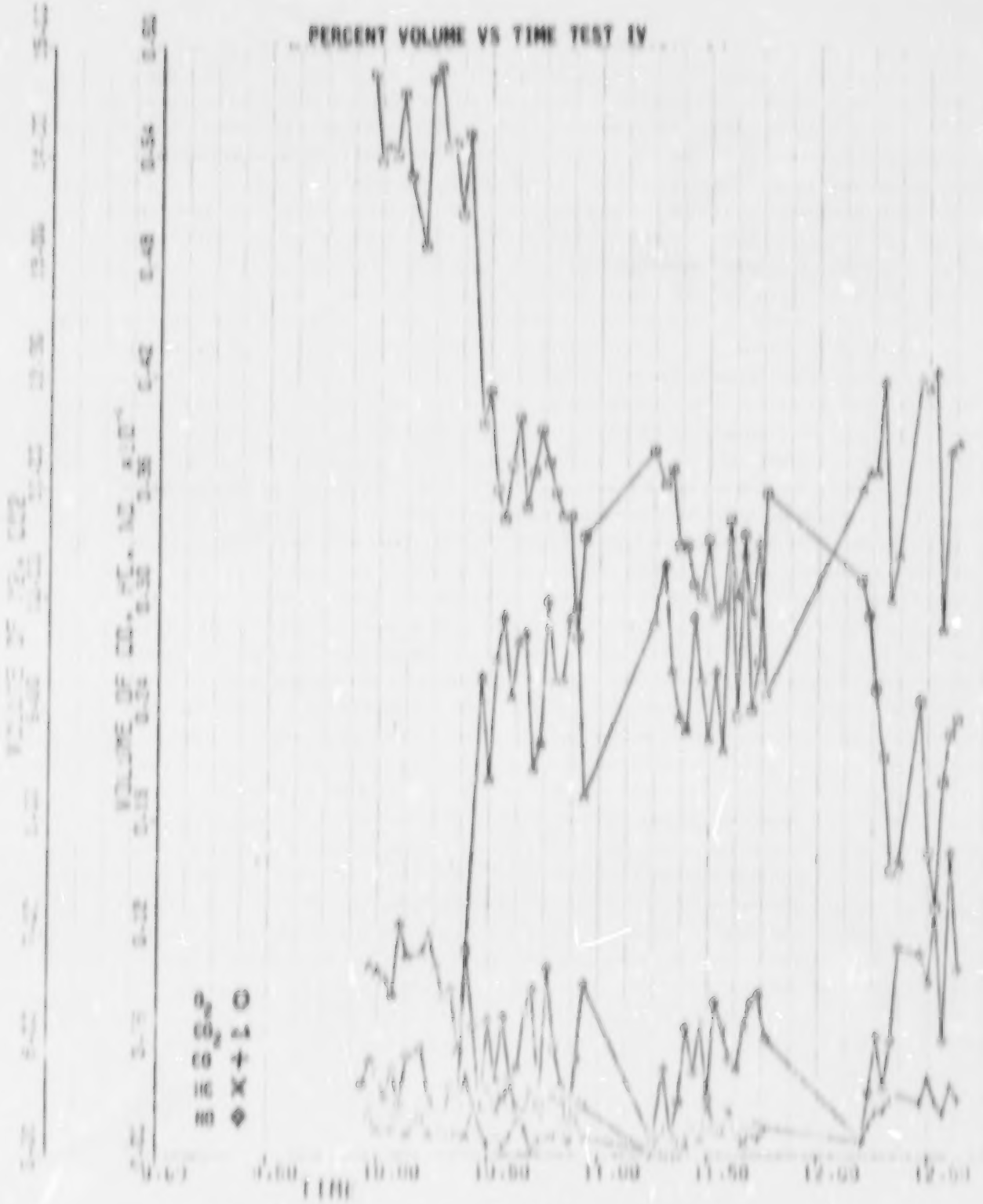

Figure 4-3. On-line gas composition data - Test IV, March 9

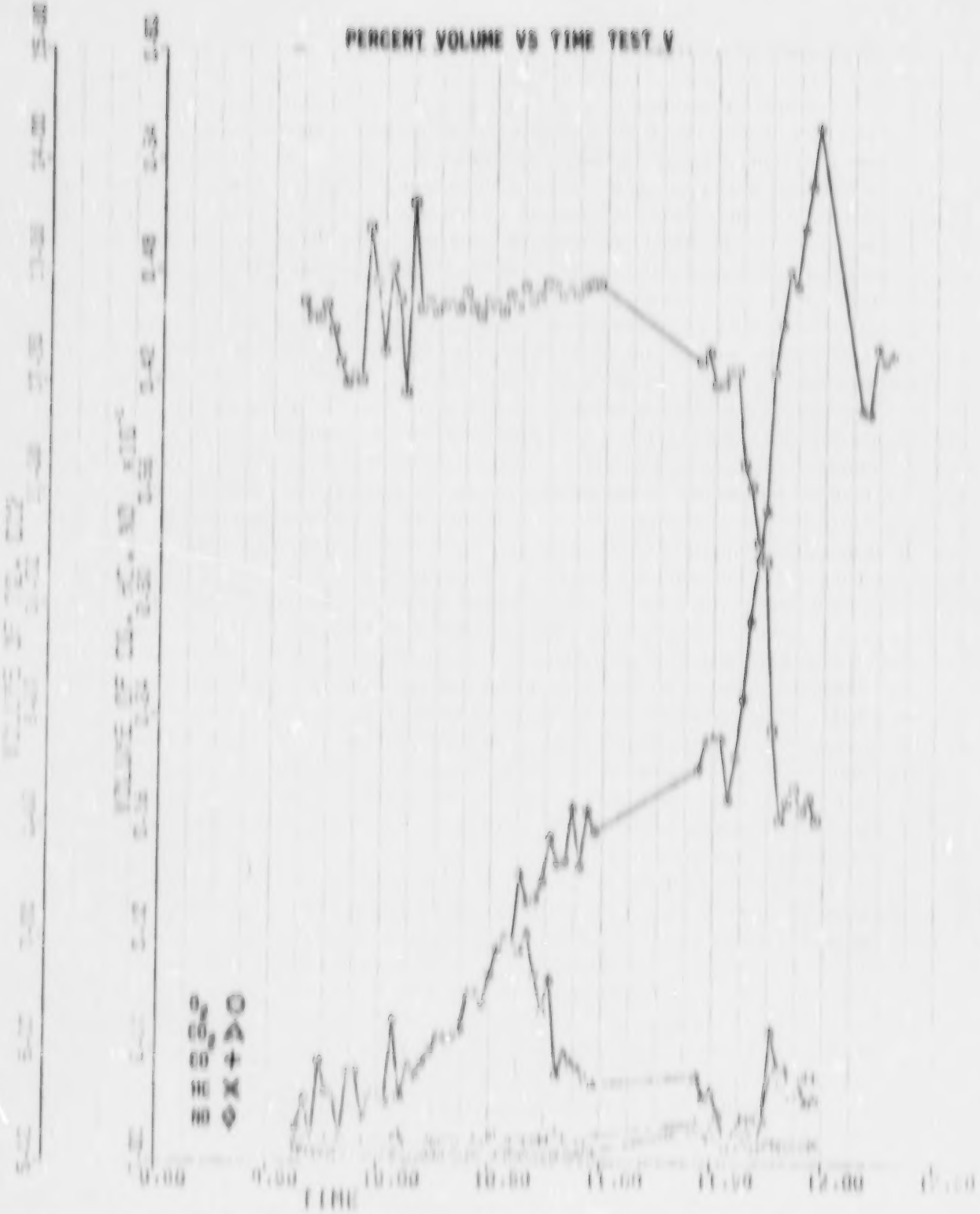

Figure 4-4. On-line gas composition data - Test V, March 10

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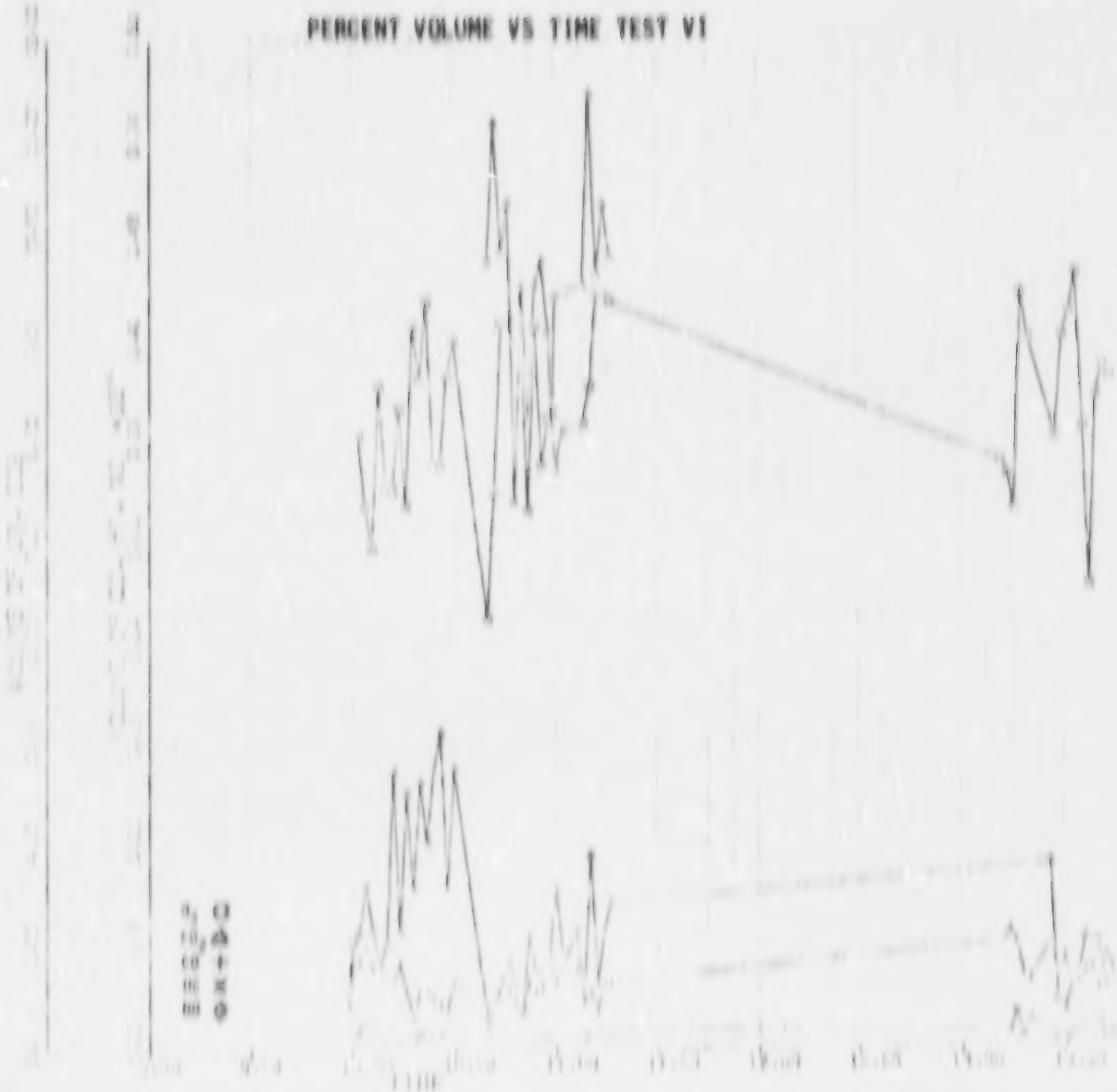


Figure 4-5. On-line gas composition data - Test VI, March 11

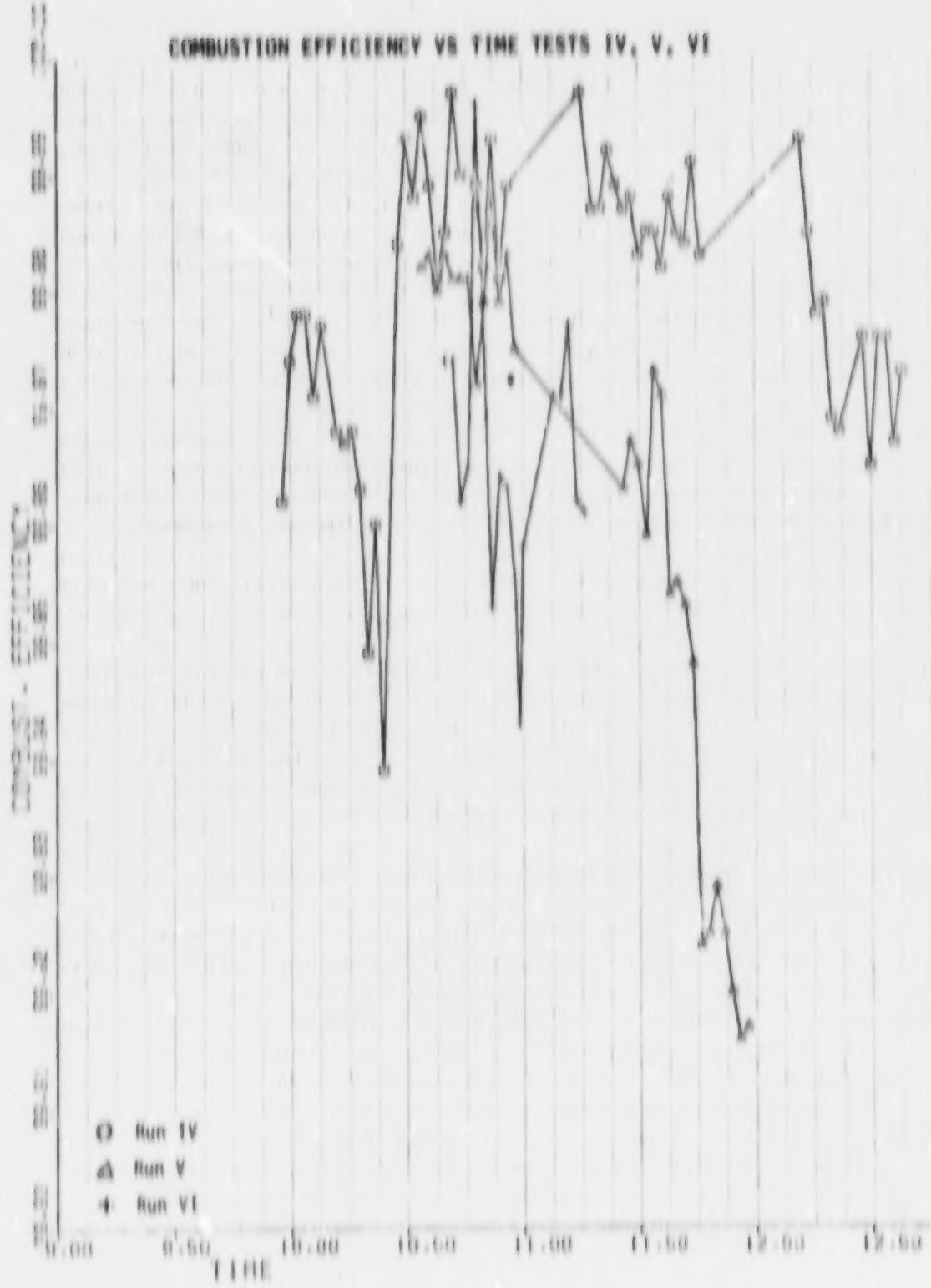


Figure 4-6. Combustion efficiency data - Tests IV, V, and VI (March 9, 10, and 11, respectively)

The data for combustion efficiency (Figure 4-6) were next examined for effects of varying probe position. To do this, an average combustion efficiency was computed from the series of readings taken each 2 minutes while the probe remained at a single position. This provided a series of combustion efficiency averages versus probe position for tests IV, V and VI, as shown in Figure 4-7. The numbers adjacent to each point on the graph indicate the number of 2 minute readings averaged and included in that particular point. Figure 4-7 indicates that combustion efficiency was 99.96% or greater except when the probe was less than 40 cm (16 in) from the incinerator wall. The 99.92% combustion efficiency calculated at 15 cm (6 in) from the wall may have been affected by ambient air leakage through the sampling port around the probe.

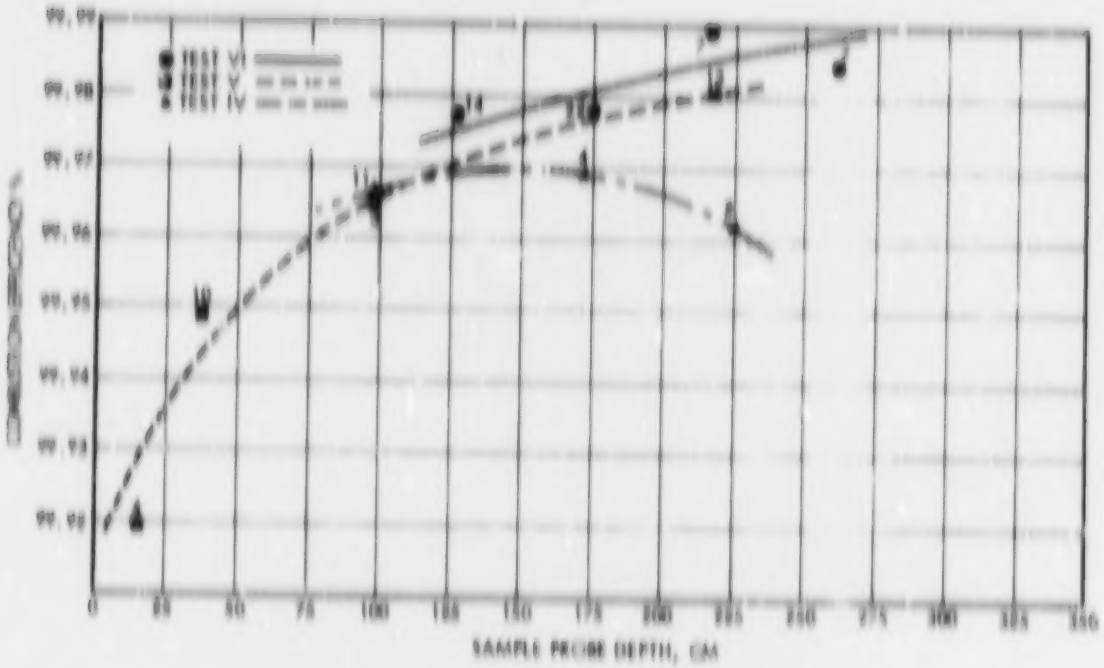


Figure 4-7. Combustion efficiency vs. probe position.

Since the combustion efficiencies plotted in Figure 4-7 were calculated from the CO_2 and CO measurements at each probe position, the CO_2 and CO concentrations versus probe position were then evaluated (Figures 4-8 and 4-9, respectively). These data indicate that both CO_2 and CO concentrations varied more from test to test than as a function of probe position, except for the CO data at 15 cm from the incinerator wall. CO increased significantly when the probe was close to the wall during Test V, as shown in Figure 4-7. These data suggest that incinerator combustion efficiency could have been measured with a fixed position probe which extended some distance greater than 15 cm into the furnace. All CO/CO_2 measurements beyond this point yielded efficiency calculations equal to or greater than 99.9 percent.

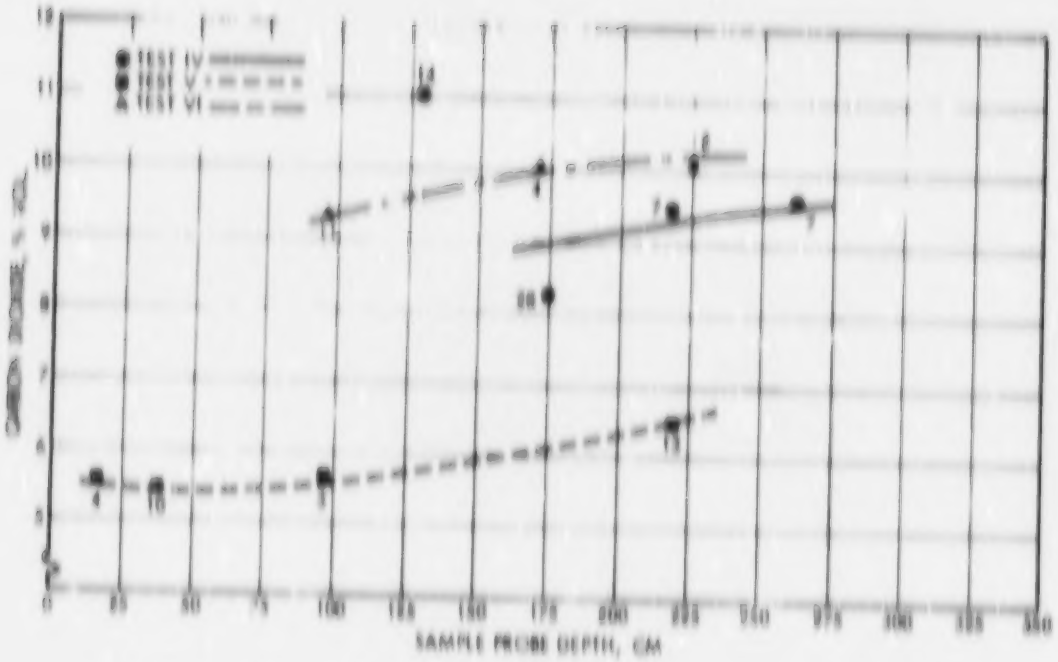


Figure 4-8. CO_2 concentration vs. probe position

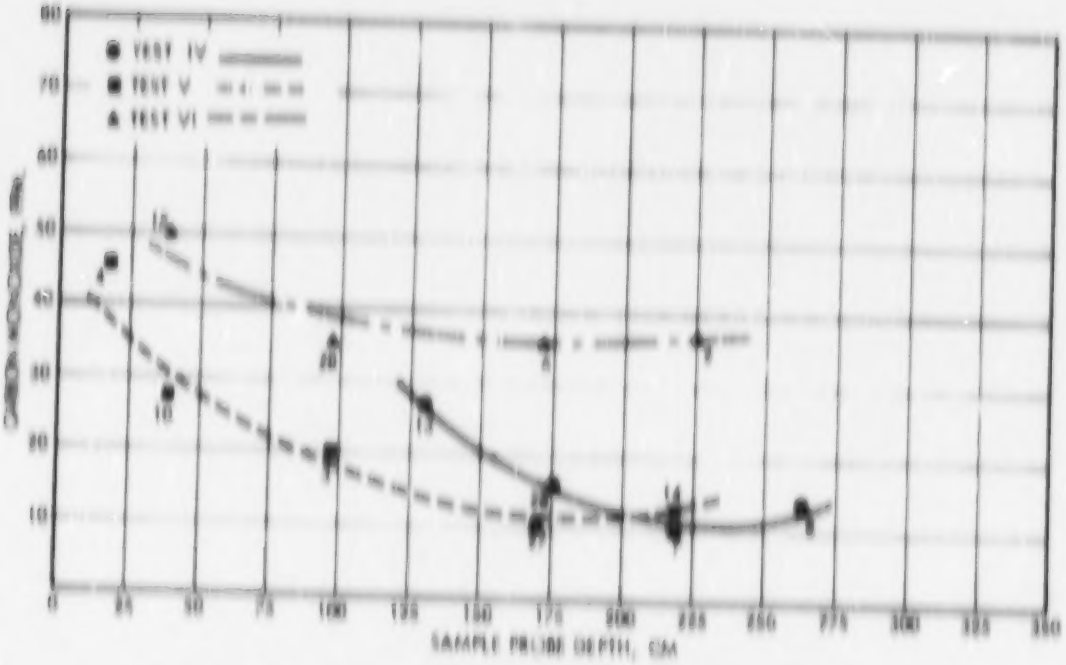


Figure 4-9. CO concentration vs. probe position.

4.1.4 Plume Characteristics

The plume from the Vulcanus was typical of the combustion of an organochloride. Under conditions of high humidity and a fairly strong breeze (>6 meters/second), the plume was observed to "touch down" 100-200 meters downwind of the ship. This behavior was observed to be general over a range of 999 to 1009 millibars (mb), 75-96% relative humidity (RH), and 5-17 m/sec wind velocity.

When the wind velocity decreased below 5 m/sec and the RH fell below 75-80%, the plume became diffuse, stayed aloft, and often became invisible. At this time the addition of ammonia gas through a standpipe between the stacks and at the plane of the stack outlets produced a visible plume of ammonium chloride. The plume could thus be traced when conditions prevented droplet condensation involving HCl gas. When the humidity was high (i.e., above 75-80%) and the wind velocity was low, the plume was voluminous, white and dense and remained aloft. Under these conditions, touch down was not observed for an estimated 5-10 miles.

The threshold conditions for aerosol formation for HCl-water vapor systems have been studied (Reference 6). In general, the requirements for visible HCl droplet formation and growth, i.e., a visible plume, are 78% RH minimum, nuclei of NaCl or NH_4Cl of approximately 0.02 μ diameter to provide condensation localities, and HCl in the vapor around the condensing droplets. When water condensation occurs, a mist will form regardless of the HCl concentration in the vapor. Conversely, if no condensation of water occurs, no mist will form, even if HCl is present in large amounts. Personnel of the M/T Vulcanus stated that a visible plume was always obtained when burning a European waste in the North Sea, as opposed to the diffuse plume discussed above. The reasons for this difference are not obvious at this time. Analyses of the two wastes showed the European waste to contain 5.4% hydrogen and 40% chlorine, while the Shell waste contained 4.2% hydrogen and 63% chlorine. Thus the Shell waste would be expected to yield combustion products lower in water content and higher in HCl content than the European wastes. However, this difference does not necessarily completely explain the lack of a plume in the Gulf of Mexico.

4.1.5 HCl Measurements on Board

Some combinations of wind velocity, wind direction and ship attitude resulted in contact of the plume with the decks of the ship. Even when the plume was not evident, it was occasionally possible to detect the presence of HCl, both by its odor and by direct measurements for HCl with Drager detection tubes. This behavior lead to consideration of atmospheric conditions and ship-wind combinations which must be avoided if contact of the plume with the ship is to be minimized. Table 4-4 lists these conditions. The wind forces listed in this table of from 6-17 meters/second correspond to velocities of 12-34 knots (1 knot = 1/2 m/s). Matching the ship's speed to a vectored velocity of the wind in the ship's direction produced a plume which remained aloft and which results in HCl values on the ship of zero

TABLE 4-4. [illegible]

Date	Time (see Figure 4-1)	Location	Relative humidity (%)	Sky condition	Wind Direction-Velocity	Temperature (°F)	Conc. HCl (ppm)
2/5/77	1000	[illegible]	60	50%	130°-6 kts	1002	1.5
		[illegible]	-	-	-	-	
		[illegible]	-	-	-	-	1
		[illegible]	-	-	-	-	1
2/10/77	1045	[illegible]	65	50%	140°-11 kts	1007	0
		[illegible]	-	-	-	-	
		[illegible]	-	-	-	-	4
		[illegible]	-	-	-	-	2
	1400	[illegible]	60	50%	150°-10 kts	1006	3
		[illegible]	-	-	-	-	
		[illegible]	-	-	-	-	2
		[illegible]	-	-	-	-	1
	1700	[illegible]	60	100%	130°-8 kts	1002	2
		[illegible]	-	-	-	-	
		[illegible]	-	-	-	-	6
		[illegible]	-	-	-	-	1.5
		[illegible]	-	-	-	-	3
2/11/77	1000	[illegible]	60	50%	140°-12 kts	999	0
		[illegible]	-	-	-	-	
		[illegible]	-	-	-	-	2
		[illegible]	-	-	-	-	4
	1340	[illegible]	55	100%	140°-12 kts	999	2
		[illegible]	-	-	-	-	
		[illegible]	-	-	-	-	0
		[illegible]	-	-	-	-	0
		[illegible]	-	-	-	-	0

[illegible]

The various locations where the Drager HCl samples were taken are marked on the plan of the M/T Vulcanus shown in Figure 4-10. The downwind (lee) side of the ship showed HCl-positive data. No HCl was detected on the windward side.

4.2 ANALYTICAL RESULTS

Of the six waste incineration sampling tests, sampling train malfunctions in the first three tests limited the sampling duration to less than one hour. Consequently, waste incineration tests IV, V, and VI, with sampling durations in excess of two hours, were selected for the detailed laboratory analyses. In addition, samples acquired from Tests VII, the background run burning fuel oil alone, were also analyzed as a baseline test for comparison to the waste incineration tests. A test and sample summary is presented in Table 4-5, and the results from analyzing these tabulated samples are presented and discussed in this section.

4.2.1 Waste Feed Analysis Results

This section presents the results of the organic and elemental characterization of the representative waste feed samples taken during each test.

4.2.1.1 Organic Constituents

Neat samples of the blended waste feed (BWF) from each test were analyzed on a gas chromatograph equipped with a flame ionization detector (FID) and an OV-17 column (see Section 3.3 for details of the procedure). The chromatograms were examined and there was a peak-for-peak, shoulder-for-shoulder match for each sample. Therefore, a careful analysis of any one of the BWF samples was applied to all of the representative waste feed samples. The representative sample from Run IV was chosen for the detailed analysis.

The composition of the waste is presented in Table 4-6. Qualitative identification of the waste constituents was accomplished by GC/MS while quantification was made on the basis of the GC analyses using the flame ionization detector (FID). The percentages have been adjusted slightly to reflect the fact that trichloropropane was present at 20 percent on the basis of direct calibration for that compound. (Trichloropropane is used as the basis for one of the waste destruction efficiency calculations this is discussed in Section 1.)

4.2.1.2 Elemental Characterization and Estimated Emission Rates

In order to estimate the hourly elemental emission from the waste incineration, duplicate samples of the Shell waste were surveyed for elemental content. The waste samples from each day of testing were first blended; then two aliquots of this blend were combusted over nitric acid in a Parr bomb. The resulting solutions were analyzed by spark source mass spectrometry (SSMS) which is a semi-quantative survey technique. The major inorganic constituents (approximately equal to or greater than 500 ppm) were calcium, chlorine, magnesium, phosphorus, and sodium. Other trace elements found are reported in Table 4-8. The average detection limit for those elements not discovered in these waste samples was 0.5 ppm.

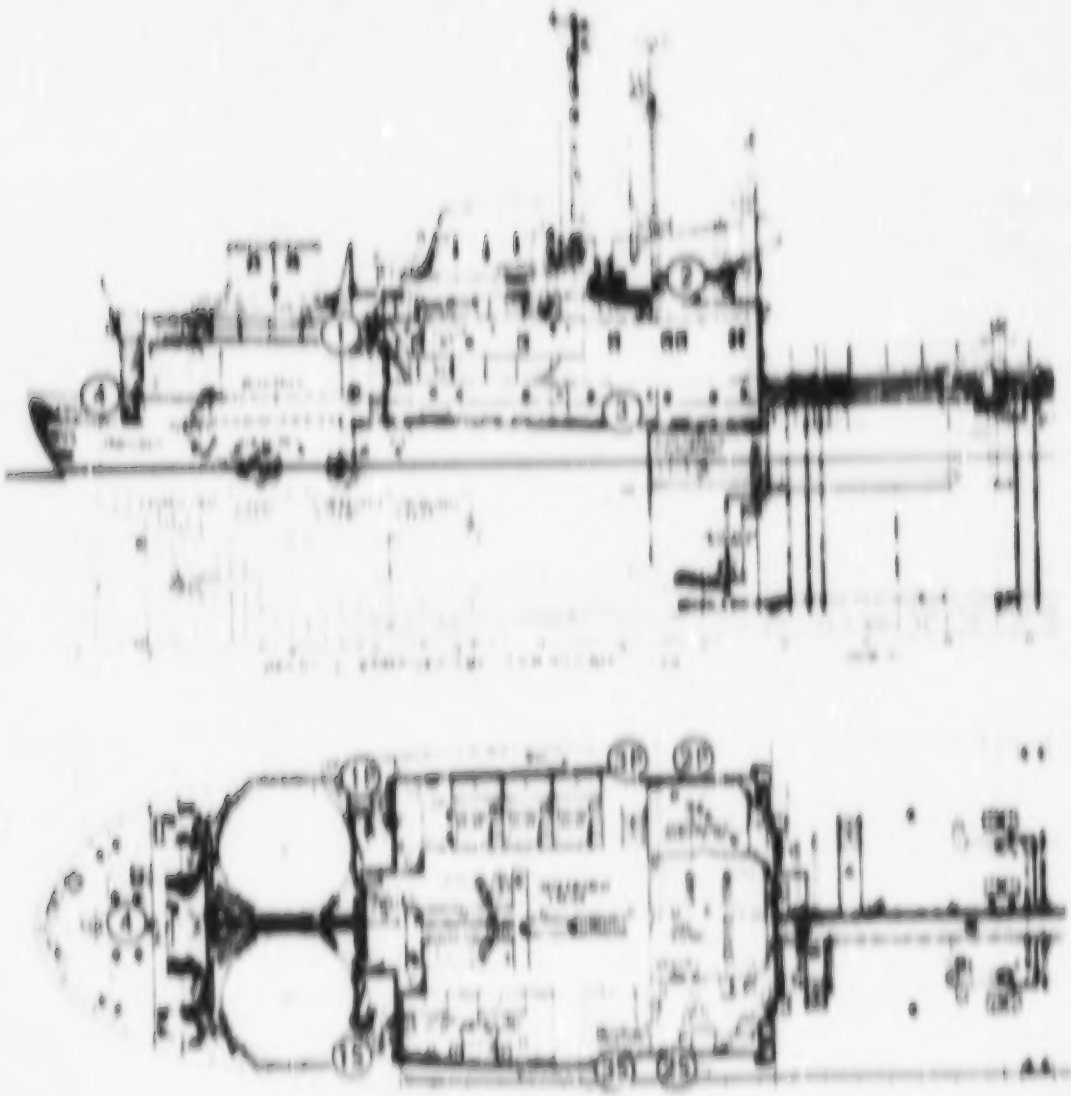


Figure 4-10. HCl sampling locations
1) combustion deck 2) bridge 3) main deck 4) stern

TABLE 4-5. SUMMARY OF VULCANUS SAMPLES

Test Number	IV	V	VI	VII
Date of Test	3/9/77	3/10/77	3/11/77	3/13/77
Length of Sampling Time (min.)	150	160	150	180
Volume of Gas Sampled (dry std. m^3)	12.5	13.4	12.1	15.8
Moisture in Gas Sample (vol. %)	15.2	15.4	20.0	9.3
SASS Samples Collected				
Quartz Probe Liner Wash (PW)	-	-	X	X
Particulate Filter (PF)	X	X	X	X
Heat-traced Sample Line Wash (HLW)	X	X	X	X
XAD-2 Sorbent Trap (ST)	X	X	X	X
Module Trap Washes				
Water (MTW-H_2O)	X	X	X	-
Isopropyl alcohol (MTW-IPA)	X	X	X	X
Pentane (MTW-P)	X	X	X	X
Pentane/methylene chloride (MTW-PM)	X	X	X	X
Module Trap Condensate (Cond)	X	X	X	X
Combined Liquid Impinders (CLI)	X	X	X	X
Acidified split (CLI-A)	X	X	X	X
Basic split (CLI-B)	X	X	X	X
Silica Gel (L4)	X	X	X	X
Blended Waste Feed (BWF)	X	X	X	X
Tedlar Bag Samples (GS)	X	X	X	X

TABLE 4-6. REPRESENTATIVE WASTE COMPOSITION BY GC/MS

Compound	Mole %
1,1-Dichloroethane	4
Bis(Dichloromethyl)ether	7
1,2-Dichloroethane	14
1,2-Dichloropropane	27
1,2-Dichloropropene	11
Tetrachloroethylene	0.3
1,1,2-Trichloroethane	6
1,2,3-Trichloropropane	19
2,3-Dichloro-1-propanol	3
2-Chloroethylchloroformate	0.7
1,2-Bromochlorocyclobutane	0.9
1,2,3,4-Tetrachlorobutane	2
Contains 4 Cl, possibly 1,2,3,3-Tetrachloropropene	0.5
Possible 2,3-Dichloro-2-methylpropionaldehyde	0.3
Halogenated, unknown, MW at least 141	0.5
2-Bromo-1,2-dichloropropane	1
Halogenated, MW at least 189	2

TABLE 4-7 PRELIMINARY SCREENING OF ON-SITE CONTAMINANTS

Chemical	Concentration in Water (ppm)	Concentration in Soil (ppm)	Chemical	Concentration in Water (ppm)	Concentration in Soil (ppm)
Benzene	0.0	0.0	Acetone	0.0	0.0
Chlorobenzene	0.0	0.0	Methylene Chloride	0.0	0.0
Ethylbenzene	0.0	0.0	Methyl Ethyl Ketone	0.0	0.0
Toluene	0.0	0.0	Methyl Isobutyl Ketone	0.0	0.0
Xylenes	0.0	0.0	Carbon Disulfide	0.0	0.0
Phenol	0.0	0.0	Vinyl Acetate	0.0	0.0
2-Chlorophenol	0.0	0.0	1,1-Dichloroethene	0.0	0.0
2,4-Dichlorophenol	0.0	0.0	1,2-Dichloroethene (total)	0.0	0.0
2,4,6-Trichlorophenol	0.0	0.0	Chloroform	0.0	0.0
Pentachlorophenol	0.0	0.0	1,2-Dichloroethane	0.0	0.0
Naphthalene	0.0	0.0	2-Butanone	0.0	0.0
Acenaphthylene	0.0	0.0	Vinyl Chloride	0.0	0.0
Acenaphthene	0.0	0.0	Chloroethane	0.0	0.0
Fluorene	0.0	0.0	Methylene Chloride	0.0	0.0
Phenanthrene	0.0	0.0	1,1-Dichloroethane	0.0	0.0
Anthracene	0.0	0.0	1,2-Dichloroethane (total)	0.0	0.0
Fluoranthene	0.0	0.0	2-Hexanone	0.0	0.0
Pyrene	0.0	0.0	Bromoform	0.0	0.0
Benzo(a)anthracene	0.0	0.0	Styrene	0.0	0.0
Chrysene	0.0	0.0	1,1,2,2-Tetrachloroethane	0.0	0.0
Benzo(b)fluoranthene	0.0	0.0	Tetrachloroethene	0.0	0.0
Benzo(k)fluoranthene	0.0	0.0	1,1,1-Trichloroethane	0.0	0.0
Benzo(a)pyrene	0.0	0.0	1,1,2-Trichloroethane	0.0	0.0
Indeno(1,2,3-cd)pyrene	0.0	0.0	Trichloroethene	0.0	0.0
Dibenz(a,h)anthracene	0.0	0.0	Trichlorofluoromethane	0.0	0.0
Benzo(g,h,i)perylene	0.0	0.0	Dichlorodifluoromethane	0.0	0.0
Aldrin	0.0	0.0	Chloromethane	0.0	0.0
Dieldrin	0.0	0.0	Bromomethane	0.0	0.0
Chlordane	0.0	0.0	Bromodichloromethane	0.0	0.0
4,4'-DDT	0.0	0.0	Dibromochloromethane	0.0	0.0
4,4'-DDE	0.0	0.0	Chloroethene	0.0	0.0
4,4'-DDD	0.0	0.0	Chloroethane	0.0	0.0
Endosulfan I	0.0	0.0	Chloroethene	0.0	0.0
Endosulfan II	0.0	0.0	Chloroethane	0.0	0.0
Endosulfan Sulfate	0.0	0.0	Chloroethene	0.0	0.0
Endrin	0.0	0.0	Chloroethane	0.0	0.0
Endrin Aldehyde	0.0	0.0	Chloroethene	0.0	0.0
Heptachlor	0.0	0.0	Chloroethane	0.0	0.0
Heptachlor Epoxide	0.0	0.0	Chloroethene	0.0	0.0
Alpha-BHC	0.0	0.0	Chloroethane	0.0	0.0
Beta-BHC	0.0	0.0	Chloroethene	0.0	0.0
Delta-BHC	0.0	0.0	Chloroethane	0.0	0.0
Gamma-BHC (Lindane)	0.0	0.0	Chloroethene	0.0	0.0
Methoxychlor	0.0	0.0	Chloroethane	0.0	0.0
Toxaphene	0.0	0.0	Chloroethene	0.0	0.0
PCB-1016	0.0	0.0	Chloroethane	0.0	0.0
PCB-1221	0.0	0.0	Chloroethene	0.0	0.0
PCB-1232	0.0	0.0	Chloroethane	0.0	0.0
PCB-1242	0.0	0.0	Chloroethene	0.0	0.0
PCB-1248	0.0	0.0	Chloroethane	0.0	0.0
PCB-1254	0.0	0.0	Chloroethene	0.0	0.0
PCB-1260	0.0	0.0	Chloroethane	0.0	0.0

Approximate mass emission rates were calculated by multiplying mg/kg (ppm) concentrations by the average feed rate of the waste (22,000 kg/hr). Thus a metal present at 10 ppm in the waste would be emitted at approximately 0.22 kg/hr. These calculated emission rates are also included in Table 4-8. Emission rates for the major inorganic constituents (Ca, Cl, Mg, P, and Na) were >10 kg/hr. Total emissions can be estimated by multiplying the above rate by the duration of the burn.

4.2.2 SASS Train Sample Analysis Results

This section describes the results of the analysis performed on the samples removed from the SASS train. Table 4-6 summarizes the samples and their sources. Direct analysis for known and expected waste constituents was made by combined gas chromatography/mass spectrometry (GC/MS). Additionally, a survey analysis was made wherein an aliquot of each sample extract was evaporated, the residue weighed, and qualitative analyses made on the residue using infrared (IR) and low resolution mass spectrometry (LRMS). These methods are described in Section 3.3.2.

4.2.2.1 GC/MS Analysis

Combined gas chromatography/mass spectrometry (GC/MS) was used for the direct analysis of the appropriate samples for known waste constituents. The samples were the solvent extracts and/or concentrates of the SASS Train components such as probe rinses, filters, line rinses, module rinses and sorbent traps. Two column systems were used:

a) Three percent OV-17 on Chromosorb W was used for all samples.

b) Chromosorb 101 was used for more effective separation of the more volatile species when they were detected using the OV-17 column.

The results of these analyses showed that only the samples from the sorbent trap and the trap module wastes contained chlorinated species. The amounts in the trap module washes were so very much lower compared to levels found in the resin extract that in summing these, the final levels for the module samples reported in Table A-8 did not change in the one significant figure reported. All four of the sorbent trap (ST) samples contained chlorinated organics. This includes the trap extract from the background test but the number of chlorinated compounds and their levels were very much less. Two reasons why the background trap extract contained chlorinated species are postulated, 1) contamination during sampling and analysis, 2) residual chlorinated material in the tanks and lines which contained the fuel oil used in the background test. No special efforts were made to identify the source of the chlorinated species found in the MV-VII background resin extract.

The list of reported compounds include some that were not found in the original waste analysis. The source of these materials may be, 1) low level waste constituents not positively identified in the waste analysis (probably less than 0.5% in the waste); 2) unexpected by-products of the incineration process; or 3) products from unknown reactions going on in the sorbent trap resin. No further work was performed to identify the source of these materials as it was considered outside the scope of the analysis task.

TABLE 4-8. EFFLUENT GAS CONCENTRATIONS FROM ANALYSIS OF SORBENT TRAP EXTRACTS (MG/M³)

Spectrum No.[a]	Assignment	IV	V	VI	VII
16	C_6H_{10}	-	0.02	-	-
35	Dichloropropane	-	0.04	-	-
51	C_9H_{18}	-	0.04	-	-
52	C_9H_{20}	-	0.02	-	-
73	$C_{10}H_{22}$	-	0.04	-	-
89	Tetrachloroethane	-	0.06	-	-
153	Tetrachloroethane[b]	0.09	0.09	0.06	-
164	Trichloropropane	0.1	0.8	0.2	-
184	Dichloropropanol	0.04	0.04	0.04	-
196	C_8 Substituted Benzene (e.g., diethylbenzene)	0.6	0.8	0.8	0.2
200	Alkyl, Oxygenated Aromatic MW 164 (e.g., Butyl Cresol)	0.1	0.1	0.1	0.1
211	C_3 Substituted Styrene	0.2	0.1	0.1	0.2
214	Unsaturated Chlorinated Hydrocarbon[b] MW 216, Possibly Tetrachlorobutene	0.1	0.5	0.1	-
238	C_8 Substituted Benzene (e.g., Triethylbenzene)	0.1	0.1	0.1	0.1
247	Tetrahydronaphthalene	0.05	0.04	0.04	-
253	C_{13} Hydrocarbon MW 258[b]	-	0.1	0.02	-
262	Chlorinated Aromatic MW 266[b]	0.07	0.1	0.05	-
266	Naphthalene (or Xylene)	0.2	0.7	0.6	0.1
271	C_4 Substituted Benzene Mixture	-	-	-	0.1
274	Chlorinated Aromatic[b]	0.02	0.04	-	-
295	Chlorinated Aromatic[b]	0.4	0.1	0.2	0.1
299	Chlorinated Aromatic[b]	0.3	0.8	0.3	0.4
340	Chlorinated Aromatic MW 320[b]	0.2	0.2	0.3	0.05
345	Dichloro, C_4 Substituted Benzene[b]	0.8	0.8	1.3	0.1
357	Dichloro, C_4 Substituted Benzene[b]	0.4	0.5	0.5	0.1
361/362	Dichloro, C_5 Substituted Benzene[b]	0.1	0.5	0.2	-
384	Trichloro C_2 Substituted Benzene[b] (MW 224)	0.2	0.2	0.2	-
390	Trichloro, Alkyl Substituted Benzene[b] (MW 238)	0.1	0.2	0.1	-
399	Trichloro, Alkyl Substituted Benzene[b] (MW 238)	0.2	0.1	0.1	-
416	Hexachlorobenzene[b]	0.08	0.04	0.05	-
	Total Chlorinated Organics, mg/m³	3	5	4	1
	Total Organics, mg/m³	5	10	8	2

a) Spectrum numbers refer to GC/MS run for Mg-1-51 which is shown in Appendix E.

b) Chlorinated compounds not confirmed as being present in the waste.

Table 4-A also presents the summation of chlorinated organics and total organics (including the chlorinated organics) found in the sorbent resin extract (ST) samples. The range of these totals is 1 to 10 mg/m^3 and corresponds to destruction efficiencies greater than 99.99%. These destruction efficiencies were not reported in the summary of this report since additional material may be present in the sample and may not have eluted from the chromatographic column. This would have lead to erroneously high destruction efficiency values.

Table 4-A contains several compounds which were only partially identified into a general class of compound. There are many reasons why partial identifications can only be made. Several of the most important are:

1) too little component to create a usable spectrum

2) unstable molecular ion which provides no molecular weight information

3) similar compounds and isomers which produce virtually identical spectra

4) time and budget limitations on the interpretation of the data

The lower limit of detectability for this analysis was established using trichloropropane standards. It was determined that trichloropropane can confidently be reported when 10 ng are injected in a 10 microliter solution volume. Within the current error limits, this detectability is presumed to be valid for all the chlorinated species found in the waste. All samples were concentrated to 10 ml; therefore, the detection limit is approximately 0.01 mg for the waste feed constituents. Even though the chromatogram for the sorbent trap (ST) extract from the background test VII is not as similar as the other ST samples from waste burns, there still is enough similarity between them to suggest that similar compounds were recovered from the sorbent trap regardless of whether the fuel was waste or No. 2 oil. This similarity is shown in gas chromatograms reconstructed from the GC/MS data (see Appendix E). The source of the commonality in extract composition likely lies in the sorbent resin and/or the manner in which it is extracted and prepared for analysis. No work was performed to investigate this situation as it was considered outside the scope of the program. In like manner, the source of the chlorinated compounds found in the sorbent resin from Test VII (background) is difficult to explain considering that fuel oil (typically with low ppm concentrations of chlorine) was the burner feed. It is also unlikely that this represents cross-contamination from the test equipment since a new probe was used and the sample lines had been flushed with pentane.

The levels of waste constituent material found in the sorbent trap module washes (MTW) was very much lower than the levels found in the sorbent traps. In fact, the levels do not exceed 0.006 mg/m^3 (1 part per billion). These amounts are only about 1 to 2 percent of the amount found in the sorbent traps. Considering the overall accuracy of the analysis and the number of significant figures in the results in Table 4-B, the trace amounts found in the module washes were not tabulated. They also do not affect the calculated waste destruction efficiencies. GC/MS analysis of the probe rinse samples found no waste constituents or other chlorinated organics.

4.2.2.2 Gravimetric Analysis

The gravimetric results, listed in Table 4-9 show the distribution of nonvolatile organic materials through the SASS train. The majority of the material appeared in the IPA module rinse, the first solvent used in the series of rinses. However, due to the polarity of this solvent, a question arose as to the possible presence of inorganics in these IPA samples. Thus thermal gravimetric analysis (TGA) were performed which showed 20 to 40 percent residues remaining at 900°C. On the basis of the TGA results, the IPA samples were assumed to be ~70 percent organic on the average, and the values in Table 4-9 were adjusted on that basis.

TABLE 4-9. GRAVIMETRIC RESULTS ON ORGANIC SASS SAMPLES

Sample Description	Test IV	Test V	Test VI	Test VII
Filter extract, mg	0.00	0.70	0.00	0.00
Heat-traced line rinse plus XAD-2 resin extract, mg	120	110	97	17
Condensate extract, mg	0.00	0.00	1.1	0.01
Water module rinse extract, mg	0.00	0.00	0.00	-[a]
Pentane module rinse plus pentane/ methylene chloride module rinse, mg	0.00	1.4	0.92	48
Isopropyl alcohol module rinse, mg	130[b]	510[b]	480[b]	490[b]
Total, mg	460	620	580	560

a) No sample taken.

b) Values are 70 percent of numbers obtained by gravimetry. Adjustment was made on the basis of TGA data showing the IPA rinses to be 60 to 80 percent inorganic materials.

The only other significant source of nonvolatile organics from the SASS train was the combined XAD-2 resin extracts and heat-traced line rinses. In particular, no significant amount of organics were collected in the filters, water module rinses, or module condensates. The rinse of the probe used for the waste tests contained only 6 mg of nonvolatile organics and the rinse of the background test probe contained no non-volatile organics. The 6 mg of non-volatile organics is especially insignificant when one considers the volume of gas that passed through that probe (~60 m^3).

4.2.2.3 Infrared Analysis

The infrared analysis qualitatively identified chlorinated hydrocarbons in the following samples: the sorbent trap module IPA wash from Test VI, and the XAD-2 resin extracts (combined with heat-traced sample line washes) from Tests IV, V, and VI. Also present in the sorbent trap

module IPA wash samples from Tests V and VII were an inorganic acid and a hydrocarbon. The pentane/methylene chloride sorbent trap module washes from Tests VI and VII contained a secondary alcohol (glycol).

4.2.2.4 Low Resolution Mass Spectrometry Analysis

Samples for LRMS analysis were selected on the basis of the gravimetric results. In general, any sample from Tests IV, V, VI, or VII with a residue weight of 100 µg or more was analyzed. The analysis was performed using the direct inlet or solids probe technique. The analytical details are found in Section 3.4.2. The objective of this kind of qualitative analysis is to determine if there is anything present in the samples which, because of its functional group composition or compound class, might be considered hazardous (e.g., chlorinated compounds, polynuclear aromatics, etc.) and require further examination using more sophisticated methods.

All compounds discussed in this section were identified from their spectral patterns, which must be extracted from the other spectral information caused by other compounds in the sample. It is therefore possible that these compound identifications are not entirely correct in every case. For example, chlorinated compounds are usually easy to detect due to the isotopic pattern of the chlorine atom; however, exact compound identification can be elusive.

To summarize the LRMS results, nearly all of the samples contained HCl and H_2O. Most of the samples contained a group of materials that have been found as artifacts in the majority of samples from previous incinerator sampling work. These ubiquitous materials consist of phthalic acid esters, hydrocarbon oils, fatty acid compounds (soap), and glycols. These easily identified substances are of little significance in the assessment of the process performance. There were some aromatic and halogenated species detected and these are listed in Table 4-10. Although they were found mainly in the sorbent trap extracts, some were also observed in the heated line washings and the module trap washings. The majority of these compounds would also be seen and more properly identified in the GC/MS analysis of the same unevaporated samples, with the exception of the benzoic acid and the C30 phenyl compounds.

4.2.2.5 Analytical Recovery for SASS Train Samples

Two samples were prepared to determine the analytical recovery. One milligram of the waste feed was added to an unused sorbent trap canister. A water sample doped with 1mg of waste feed was also prepared to which HCl and iron, nickel and chromium salts were added. This stimulated both the condensate solution and the aqueous sorbent trap module washes. This aqueous sample was split and one part was neutralized to pH7 with sodium hydroxide to simulate the manner in which the aqueous samples were treated in the analysis. Of the compounds present in the waste, only trichloropropane was found in these doped samples by GC/MS analysis. This is not

TABLE 4-10. LRMS RESULTS ON ORGANIC SASS SAMPLES

Sorbent Trap	Heated Line Wash	Sorbent Module Wash
Chlorotoluene	Chlorotoluene	Chlorotoluers
Dichloro isopropyltoluene Benzoyl chloride	A highly fluorinated chlorobutane (possibly tetrachlorohexafluorobutane)	A highly fluorinated chlorobutane (possibly techtrachlorohexafluorobutane)
Benzoic acid		
Butyl aniline	C_{16} or C_{17} compound, $\approx$206	C_{16} or C_{17} compound $\approx$206
C_{30} phenyl compound		
Dimethyl allene phosphonic acid		
Mixed benzoates		
Ethyl benzaldehyde		

surprising at the levels at which the control samples were doped. Trichloropropane is one of the major waste constituents, and many of the lesser species did not exceed our estimated detection threshold. Recoveries based on trichloropropane are reported in Table 4-11.

TABLE 4-11. ANALYTICAL RECOVERY FOR SASS SAMPLES

	Trichloropropane Added (ug)	Trichloropropane Found (ug)	Recovery (Percent)
Sorbent Trap	200	220	110
Sorbent Module Condensate	100	60	60
Sorbent Module Condensate Neutralized	100	40	40

Another source of sample loss is that constituents may be lost in the concentration steps. These samples were concentrated up to one hundredfold using the fractional distillation process of a Kuderna-Danish evaporator. Any waste constituents which have a higher vapor pressure than the pentane, acetone or isopropanol solvents will be preferentially lost. Moreover, some of the less volatile compounds may

be partially lost due to the incomplete effectiveness of the fractional distillation column. Any or all of the sources of incomplete sample recovery may affect any of the samples which were treated.

The data reported for the sorbent trap extracts in Table 4-8, were not corrected for analytical recovery because the sorbent trap recovery sample yielded more than 100 percent; therefore no correction was required. The sorbent trap module wash samples were corrected for 40 percent analytical recovery, but they still resulted in the trace levels reported. It is stressed that these tables reflect analytical recovery changes only. Trapping efficiency for the sorbent traps was derived from the graphs in Reference 5.

4.2.3 Gas Bag Sample Analysis Results

Two analytical procedures were used to characterize these samples.

- Low Resolution Mass Spectrometry (LRMS) of the neat, as received, bag sample.
- Concentration of trace constituents using absorption on Tenax, followed by desorption and GC analysis.

4.2.3.1 LRMS Analysis

A portion of a Tedlar bag sample from each of Tests IV through VII was analyzed by low resolution mass spectrometry for:

a) Semi-quantitative composition of the major constituents, e.g., O_2, N_2, CO_2, HCl, etc.

b) Qualitative determination of levels of the chlorinated organics known to be present in the waste feed.

The major constituents are presented in Table 4-12. Comparison of the data with that from the on-line analyzers shows fair agreement with O_2, CO_2, and N_2. Though attack and degradation of nylon valves on the

TABLE 4-12. GAS BAG CONSTITUENTS BY LRMS

Test Number	Concentration, Mole Percent						
	H_2	H_2O	N_2/CO	O_2	Ar	CO_2	HCl
IV	<0.001	0.02	79.3	15.6	1.1	3.9	N/D
V	0.01	0.03	79.2	15.4	1.1	4.3	N/D
VI	0.006	0.1	79.6	10.8	1.1	8.4	N/D
VII	<0.001	0.03	79.7	14.3	1.1	4.8	N/D

N/D = Not detected. Limit of detection was 200 ppm.

Tedlar bags had occurred, this demonstrates that the gas in the bag was not ambient air resulting from leakage or other sample loss and that the bag sample integrity was adequate for analysis of residual trace chlorinated organics in the effluent stream. The low levels of HCl reported in the LRMS data can be explained by the fact that the nylon fittings on the Tedlar bags were found to have undergone hydrolytic attack by the HCl.

A search of the same data was made for all chlorinated compounds and specifically known waste constituents. However the technique was not sensitive enough to yield adequate detection limits. This led to the use of the technique discussed in the following section.

4.2.3.2 Tenax/GC Analysis

The results of the Tenax concentration and GC/FID analysis are shown in Table 4-13. Calibration for the waste constituents was performed using trichloropropane. This major constituent of the waste was used as a tracer for all waste constituents. Waste destruction efficiencies were calculated on the basis of trichloropropane analysis results.

Also presented in the table is a measure of the total organics which were detected by the FID. The levels were calculated from total GC peak area integration data. Response was determined from injections of known amounts of organic material. The ppm values are reported as methane for ease in comparing data with the on-line hydrocarbon analyzer data. These levels should not be considered to be more accurate than ±100 percent. The destruction efficiencies calculated from the trichloropropane and total organic data are discussed further in Section 1.

TABLE 4-13. GAS BAG ANALYSIS BY TENAX/GC

Test	Trichloropropane mg/m^3 (ppb)	Waste Destruction Efficiency[a] ($DE_{C_3H_5Cl_3}$)	Total Organic Material mg/m^3 (ppm as Methane)	Total Organic Destruction Efficiency (DE_{THC}) Percent
IV	<0.06 (<9)	>99.999	9 (12)	99.991
V	0.12 (21)	>99.999	106 (27)	99.991
VI	0.12 (21)	>99.999	12 (16)	99.991
VII				99.996

[a] Based upon trichloropropane as a typical waste constituent and present in the waste at 20 percent (W/W).

4.2.4 Burner Head Residue Analysis Results

The requirement for routine cleaning of the burner heads was frequent during the incineration of the waste. There was interest in characterizing the burner head residue for hazardous constituents since the residue is a potential disposal problem. A sample of the residue weighing 61.7 grams was broken up into 10-12 mesh size and extracted with pentane.

Several analyses were performed on this sample and the results are as follows:

- A 1ml aliquot of the concentrate was evaporated down just to dryness and weighed. The residue amounted to 3.6 weight percent of the original burner head sample.

- An IR spectrum was obtained of a smear of the residue and the spectrum indicated the presence of hydrocarbons and possibly some glycols. No trace of the waste constituents was found.

- The low resolution mass spectrometer (LRMS) data indicated HCl, trichloropropane, bromodichloropropane and hydrocarbon oil.

- The burner head extract was also analyzed by GC/MS. The results show that most of the compounds in the waste feed (as seen in the representative waste sample) were also present in this extract. The GC separated the mixture of the earlier eluting compounds very effectively, and most of the waste constituents were identified. The second portion of the chromatogram consisted largely of incompletely resolved peaks constituting a major portion of the total response seen in the chromatogram. The general character of the compounds in this higher boiling portion of the mixture shown by their spectra was that of aromatic compounds, some of which were chlorinated. Intensive effort to completely separate and identify each compound in the mixture was not carried out due to budget and schedule considerations. Complete quantification is not achievable for an additional reason, which is that much of the material in the weighed residue discussed above is likely to be polymeric "tars", an unknown portion of which is not likely to elute from a gas chromatograph. The identified compounds and their calculated concentration (wt/wt) in the burner head scrapings are presented in Table 4-14. The reconstructed chromatogram of this sample is shown in Appendix E.

TABLE 4-14. COMPOUNDS FOUND IN BURNER HEAD RESIDUE

Compound	Concentration in Burner Residue mg/kg
Dichloroethane	15
Dichloropropane	70
Dichloropropene	50
Trichloroethane	85
Trichloropropane	120
Dichloropropanol	115
bis(2-chloroethyl)ether	80
Tetrachlorobutane	80

5. REFERENCES

1. Wastler, T. A., et al., "Disposal of Organochlorine Wastes by Incineration at Sea," EPA-430/9/76-014, July 1975.

2. TRW Report on "Destroying Chemical Wastes in Commercial Scale Incinerators", Contract No. 68-01-2966, Facility Report No. 1, The Marquardt Co., October 1976.

3. TRW Report on "Destroying Chemical Wastes in Commercial Scale Incinerators", Contract No. 68-01-2966, Facility Report No. 6, Rollins Environmental Services, April 1977.

4. Federal Register, June 28, 1976, Part III, Environmental Protection Agency - Ocean Dumping - Proposed Revision of Regulations and Criteria.

5. Levins, P., et al, "Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds," EPA-600/7-77-044, April 1977.

6. Fenton, D. L., and Renade, M. B., "Aerosol Formation Threshold for HCl-Water Vapor Systems," Environmental Science and Technology, 10:1160-62, 1976.

APPENDIX A

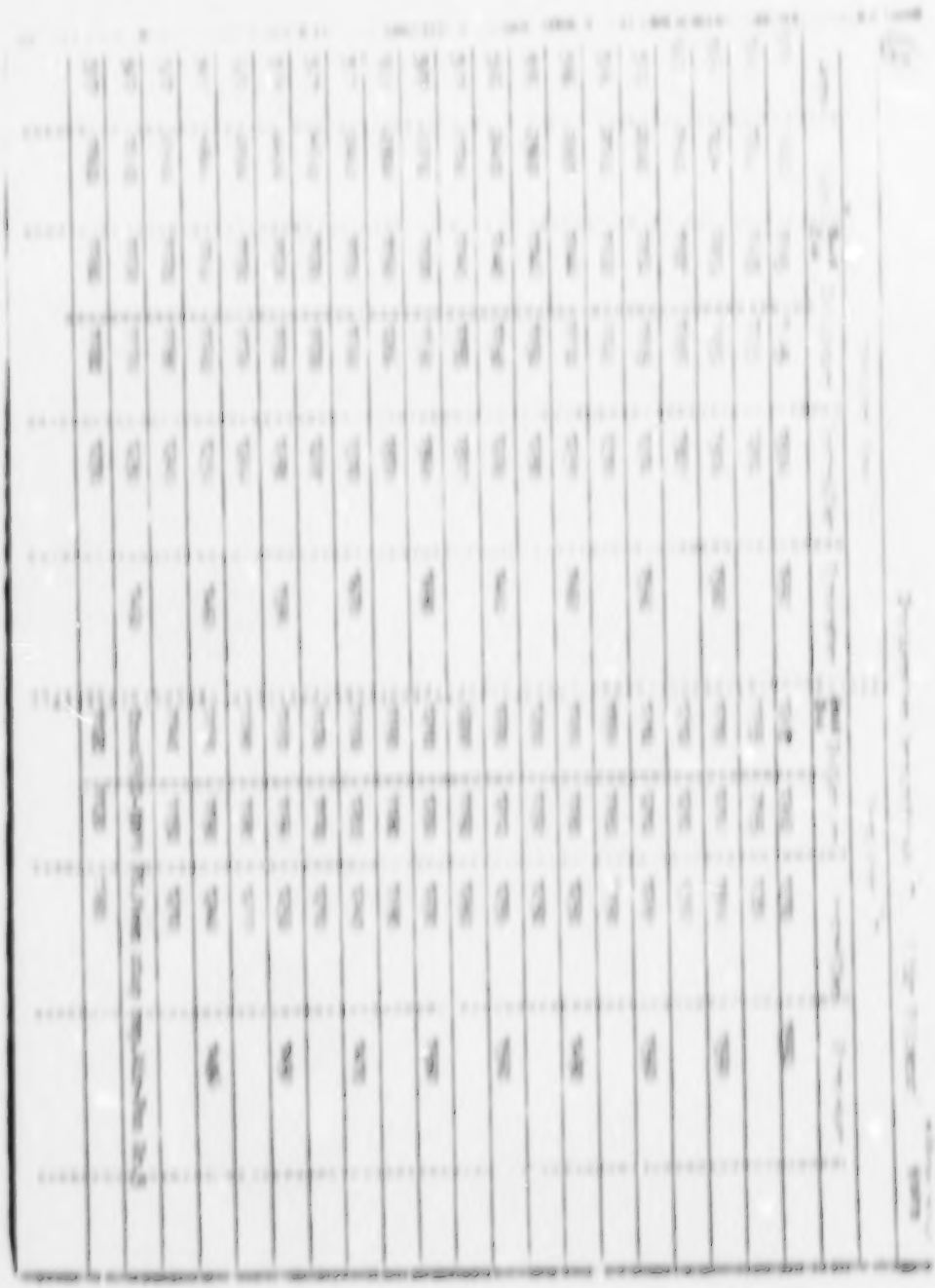
SCHEDULE OF WASTE CONSUMPTION BY TANK NUMBER AND LOCATION

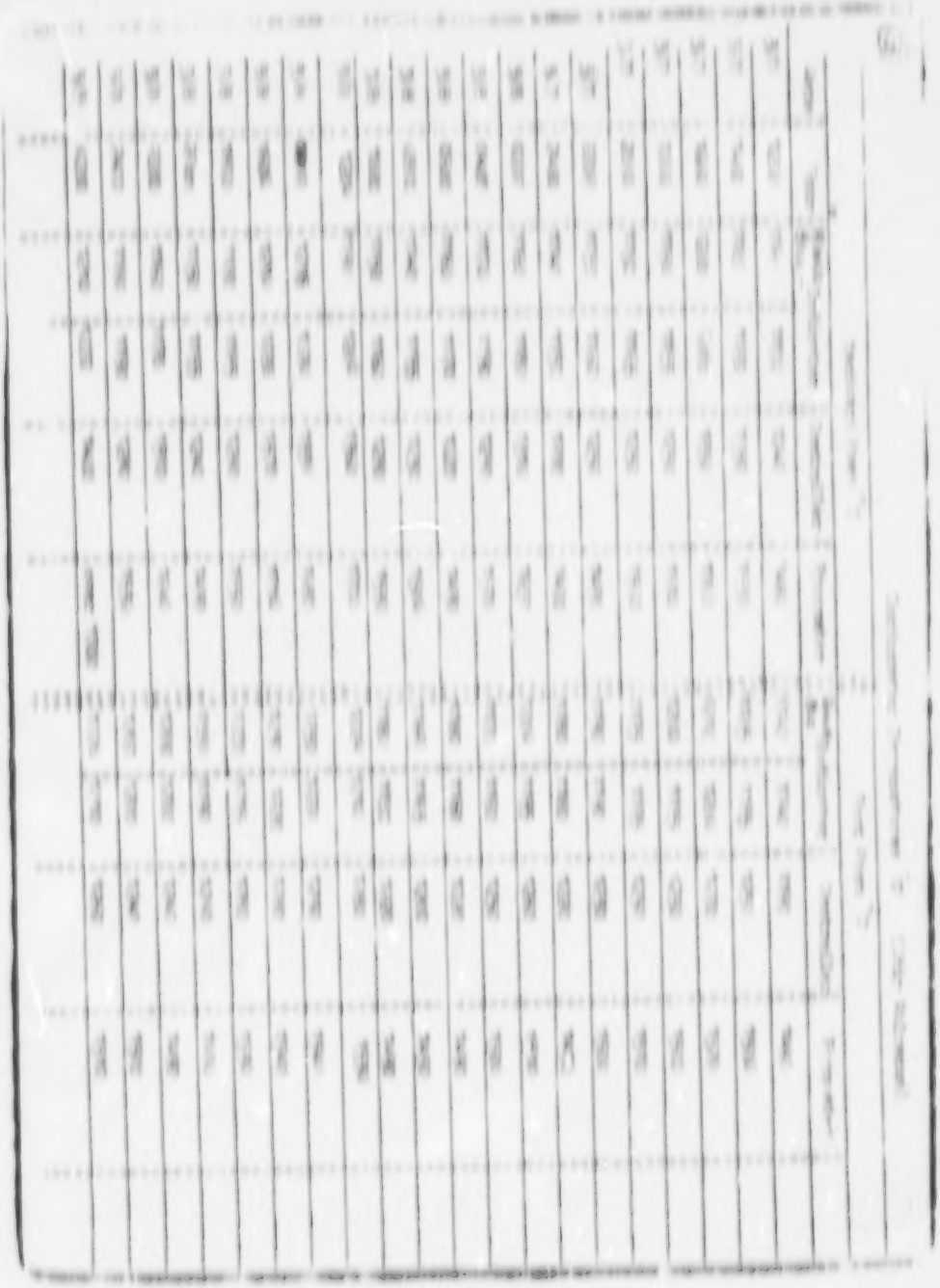
APPENDIX B

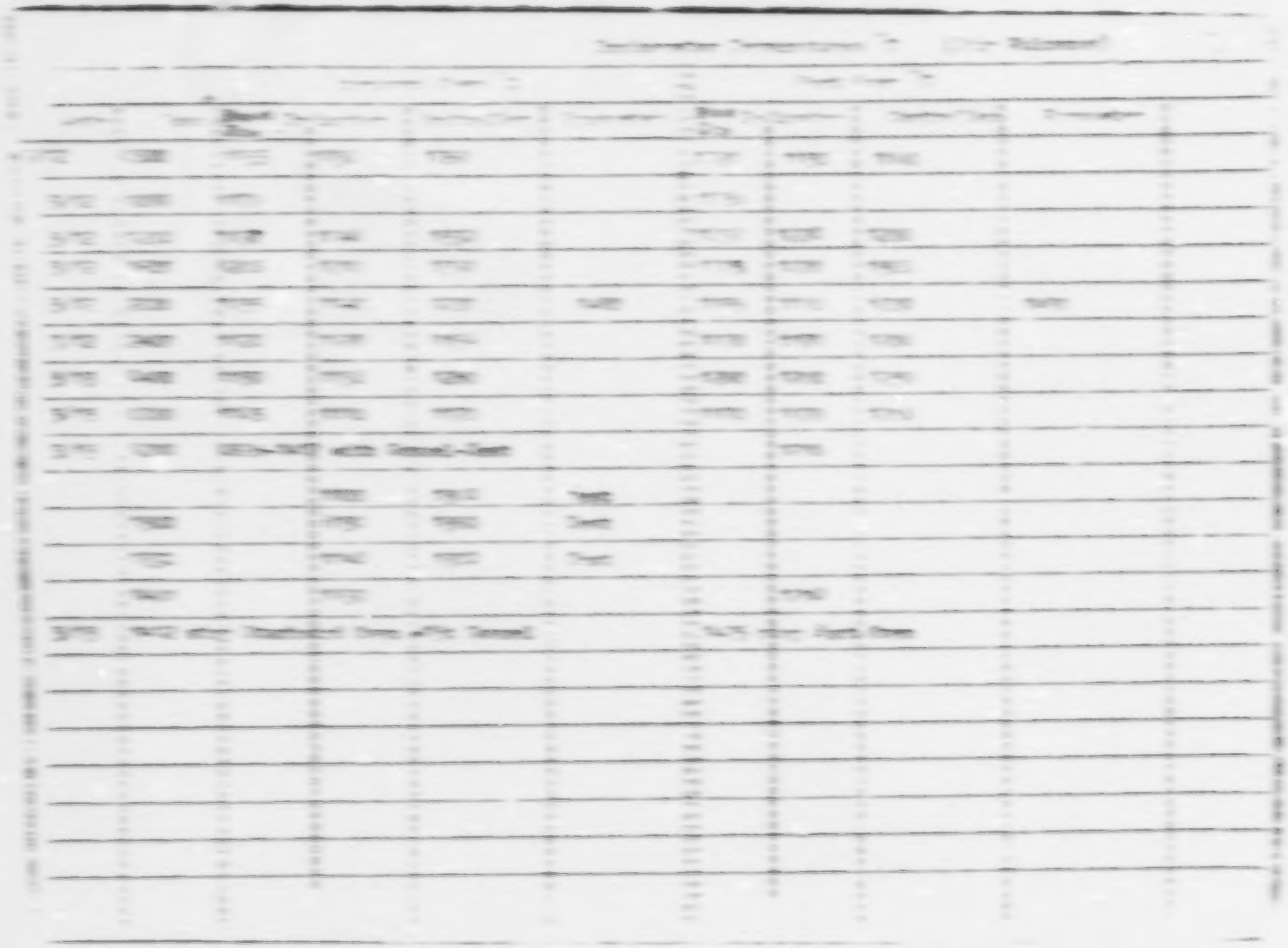
TABULATION OF TEMPERATURES IN FURNACES BY

a) Optical Pyrometer (Flame Temperature)

b) Wall Thermocouples







APPENDIX C
SAFETY PROCEDURES

VULCANUS SHIPPING CO. PTE. LTD.

TELEPHONE [illegible]
CABLES VULCANSHIP TELEX RS [illegible]

VULCANUS SHIPPING CO PTE LTD SINGAPORE 1

YOUR REF OUR REF

[illegible] ROAD AND FLOOR
SINGAPORE 1

Before loading:

1.clean perthotes on trunks
2.check deventing valves and gauging valves
3.check overflow valve and manually and plug overflow tank
4.inspect pressure/vacuum valve
5.have emergency firefighting pump tried out with two (2) hoses
6.check and try out emergency shower next to galley
7.check if all manifold,charge and discharge valves are closed
8.check if loading filters are clean
9.operate fireflaps of pump room,ventilator room and generator room
10.check on properties of cargo
11.have international shore connection ready

At loading place:

1.check international ship/shore safety check list with shore representative
2.rig up gangway with net and buoy
3.rig up fireswarpe fore and aft
4.red flag/red light
5.close scuppers
6.try out emergency shut-off valve
7.if required: dip tanks with shore representative
8.connect two(2) fire fighting hoses to the line
9.put three (3) fire extinguishers near manifold
10.have two (2) safety suits on deck
11.have two (2) safety belts and lines on deck
12.have two (2) self contained breathing apparatus on deck
13.one bucket with lid,containing salted water on deck
14.one eye-washing bottle with distilled water on deck
15.one first aid satchel on deck
16.have enough safety and protective clothing (cleaned) standing by
17.pressure on emergency shower
18.check if all sweet trunks and butterworth-holes are tightly shut
19.have ship bonded before connecting
20.connection to be made with at least four (4) bolts.Check.
21.have dripping-pan put under connection
22.check high-level alarm and on
23.have sufficient gasmasks/fumemasks with brown filters(breger) ready

Loading:

1.Contact engine department for OK loading
2.open emergency shut-off valve
3.open manifold valves
4.openall valve and check if cargo is running in the intended tank,then open acc

During loading:

1.Check tank level regularly and maintain access communication with loading-station

2.check high-level alarm regularly

if necessary a gas return line can be connected.

all personnel involved in cargo handling must wear protective clothing,boots, gloves,helmut and goggles.

As the vessel must be able to move under its own power,all repairs on the main engines must be authorised by the master,Chief Engineer, or certain and loading

General rules on safety will be found in:

Tanker Safety Guide

Petroleum Tankship Safety.

both publications are to be found in the meeting-room and must not be removed from there.

The master,

J.J.Saverda

1.In order to vent the incineratorroom properly,all ventilators must run for at least twenty (20) minutes before starting the incinerators. During this time all burners,pumps etc.are blocked by a time relais.

2.If during incineration (gasoil or chemicals) the output of a ventilator drops (insufficient air flow), a optical and accoustical alarm is given. Automatic airpressure controllers are installed on each ventilator.

3.When the flame of a burner goes out,a photocell shuts the magnetic valve before the burner and the flow of the medium is cut.

4.Should during the incineration of chemicals the temperature drop under the required level,all pumps will stop and the magnetic valves before the burners close.In that case the installation must be preheated again to the required temperature by gasoil.

5.In case of emergencies (line failure or similar) the installation can be stopped by emergency-switches.These are located:
on the access control deck in the incineration room
on the bridge
near both of the two entrances to the incineratorroom on the main deck in the crew's accomodation.
There are five (5) switches in total.

6.There is an alarm system fitted in the bilges of the pumproom.In case of line failure in the pumproom,the main discharge valves can be closed from the main deck.

7.In case of spillage in the incinerationroom the personnel must immediately don gasmasks (dräger filter brown).The same applies to entering the pumproom.

8.For protection against chemicals protective clothing,gloves and boots must be worn.An eye washingshower is situated in the incineration room.

9.The watches change every four hours and are kept by an engineer and an assistent-engineer.The pumproom and the ventilatorroom are checked hourly. The incineratorroom is constantly occupied.Between this room telephone connections exist with the bridge,engineroom,mess-room,pumproom and cabins of the engineers.

APPENDIX D

BURNER MAINTENANCE RECORD

3-5 Start with heating up 0800 (Gasoel)
2000 start with Waste combustion.

3-6 0300-0343 stop Burner Nr.5,
0300-0324 clean Burner Nr.4-5-6,
0409-0433 clean Burner Nr.1-2-3-4-5-6,
1610-1630 clean Burner Nr.1-2-3-4-5-6,
2115 Stop Gorator 2 and start Gorator 3.

3-7 0400-0420 clean Burner Nr.1-2-3-4-5-6,
0900-1010 stop PS.Oven rep.Air-Fan.

3-8 0315-0325 clean Burner Nr.1-2-3,
0608-0622 clean Burner Nr.4-5-6,
0624-0635 clean Burner Nr.1-2-3,
1500-1510 clean Burner Nr.4-5-6,
1600-1610 clean Burner Nr.1-2-3,

3-9 0202-0213 clean Burner Nr.4-5-6,
0638-0650 clean Burner Nr.1-2-3,
0718-0731 clean Burner Nr.4-5-6,
0950-1020 stop Burner Nr.5 rep.E.-Valve,
1747-1757 clean Burner Nr.4-5-6,

3-10 0000-0010 clean Burner Nr.4-5-6,
0700-0714 clean Burner Nr.4-5-6,
0714-0739 clean Burner Nr.1-2-3,
1350-1425 stop Burner Nr.5 change E.-Valve,
1633-16a7 clean Burner Nr.4-5-6,
1650-1702 clean Burner Nr.1-2-3,
2357-2400 clean Burner Nr.4-5-6,

3-11 0000-0010 clean Burner Nr.4-5-6,
0010-0021 clean Burner Nr.1-2-3,
0350-0355 clean Burner Nr.5,
0615-0628 clean Burner Nr.4-5-6,
0800-0925 stop Burner Nr.4 rep.Elect,
1120-1127 clean Burner Nr.4-5-6,
1345-1355 clean Burner Nr.1-2-3,
1500-1505 clean Burner Nr.5,
1720-1725 clean Burner Nr.2,

3-12 0205-0230 clean Burner 4-5-6,
0230-0246 clean Burner 1-2-3,
1025-1035 Burner 5 with Gasoel,
1055-1108 clean Burner 4-5-6,
1500-1510 clean Burner 4-5-6,
1730-1742 clean Burner 1-2-3,
2130-2135 Burner 5 with Gasoel,

13 0250-0255 clean Burner 5,
0609-0620 clean Burner 4-5-6,
0620-0632 clean Burner 1-2-3,
0828-1412 SB.Oven with Gasoel for the test. (1St Gasoel)
1425 stop P5.Oven,
1415 stop Waste Combustion.

APPENDIX E

GC/MS RECONSTRUCTED GAS CHROMATOGRAMS